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PROCESSES FOR ASSESSING
THE THERMAL STABILITY OF
HAN-BASED LIQUID PROPELLANTS,
FINAL REPORT

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13. ABSTRACT (Maximum 200 words) Liquid Propellants containing hydroxylammonium nitrate (HAN) react with metallic and non-metallic impurities. Two tests were developed to monitor gas evolution during storage at 90° C in 5-cc sealed glass ampoules or 3-cc glass containers fitted with miniature pressure transducers. Time to bursting of the ampoule or to a specific pressure in the container are the data obtained. The propellant's stability is dependent on pH with 2.1 being optimum. The effects of numerous metals, both as elements and ions, and plastics on the stability of LGP1846 are examined. Iron, copper, and vanadium ions caused the most reaction, and vanadium shows an effect at concentrations as low as 0.5 ppm. Magnesium, zinc, and manganese ions had no effect in storage life by this test criterion. Of the 30 metals and alloys investigated, 2 gunmetals and 3 stainless steels were subject to pronounced attack, but gold, silver, and tantalum remain unaffected. Numerous aminophosphinic acids inhibit the effect of metallic impurities, and Dequest 2041 was particularly effective for iron and copper ions. Most plastics cause decomposition and/or coloring of the propellant. Only polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE) were found to be inert.				
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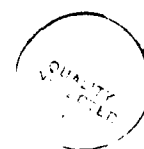
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1. INTRODUCTION

Liquid propellants that contain hydroxylammonium nitrate (HAN) as a major component contain both oxidizing and reducing ions that can react readily with many materials. Changes in either the material or the propellant would probably be deleterious. The decomposition that results adversely affects storability, handling, and performance. Gases are a usual product of decomposition and dangerous pressures in storage tanks can be obtained. The partial loss of an energetic component causes changes in ignition and combustion behavior and a decrease in performance. Furthermore, decomposition usually results in the formation of nitric acid and ammonium nitrate, both of which adversely affect propellant properties. The production of acid will reduce the pH of the mixture, a condition that will enhance reactivity and thereby further reduce storage stability. Based on the data presently available, the purest propellants have always shown the greatest degree of stability. Impurities can be introduced by reaction with components of systems utilizing the liquid propellants, as raw materials used in synthesis, or by improper handling after production. It has been possible, by means of special processes such as the electrochemical methods developed for the manufacture of HAN by Olin (Dotson 1988), to fulfill the strict demands for purity in liquid propellant manufacture. However, the introduction of impurities after production needs addressing and one aspect of our studies will deal with the possibility of stabilizing these mixtures by removal of the offending ions via the formation of coordination complexes.

Storage at elevated temperature (accelerated aging) was selected as the stability testing method with the evolution of gas as the evaluation criterion. Although the use of gas production at elevated temperature as a criterion of stability is probably theoretically sound, we chose to make relative measurements by comparing the data obtained with companion data taken with pure propellants or standard preparations. In addition, determination of reactant and product concentration by analysis of the stored samples served to correlate the validity of gas production as a measure of instability. Since the propellants are aqueous, ionic mixtures, care is required when performing storage tests at higher temperature that the composition of propellant not change due to evaporation, condensation, or absorption. Hermetically sealed test containers are therefore required. Two methods were needed to assess storage life:

- (1) An inexpensive, rapid, and safe method that would essentially screen a large number of materials.
- (2) A detailed, quantitative procedure that would generate data concerning the rate of gas production. These data could be used for kinetic evaluation of the reactions observed.

2. WORK SCHEDULE OF PROJECT DAJA 45-86-C-0056

The aim of the work was to develop thermal stability tests for the HAN-based liquid propellants that had been developed by and were in use at the Ballistic Research Laboratory (BRL), Aberdeen Proving Ground, MD, USA. The tests concerned chemical stability, the influence of impurities on storage behavior, and attempts to improve the chemical stability of the propellants through use of additives. In addition, analytical procedures had to be developed for quantitative determination of the individual components of the propellants.

The following tasks were to be addressed:

- (1) Development of quantitative analytical methods to determine the concentration of components, decomposition products, and impurities in propellant samples.
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- (3) Determine the effect of impurities, notably the ions of the transition metals, on chemical stability, generating, where possible, safe concentration limits. Both the measurement of concentration changes of the individual components and decomposition products such as NH_4NO_3 and HNO_3 and measurement of pressure as a function of time during long-term storage in sealed pressure containers at increased temperature were to be part of this effort.
- (4) Improvement of stability through optimization of propellant pH.
- (5) Attempts to improve storage life by use of stabilizers.
- (6) The measurement of gas composition after ignition in a combustion chamber subjected to increasing initial pressures is a task under this contract but will be the subject of a separate study.

Samples of propellant LGP1846, Lot 49-1, were provided by the sponsor. In addition, we prepared samples of LGP1845 and LGP1846 from HAN produced by BASF (FRG) and Thiokol (USA). Analytical data obtained for these mixtures will be presented subsequently.

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3. DECOMPOSITION MECHANISM OF LIQUID PROPELLANT COMPONENTS

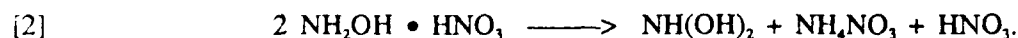
The HAN-based propellants are usually formulated to balance fuel and oxidizer at equilibrium. According to Klein (1988), the reaction occurring when the propellant is burned follows the equation:



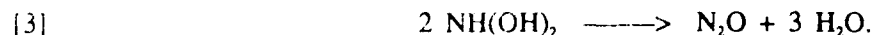
This rapid reaction is pressure dependent and will not be observed at lower pressures. Instead, a partial decomposition is obtained and the oxides of nitrogen, carbon monoxide and hydrogen are found among the products. When reacting slowly at moderate pressure, as would be the case during long-term storage, HAN decomposes to a much greater extent than TEAN, and the equation cited is not applicable for describing the decomposition processes. Consequently, reaction mechanisms that address the slow, thermal decomposition of HAN are required.

Although HAN can undergo both oxidation and reduction, it is oxygen-rich and requires a second, fuel-rich component to produce the desired oxygen balance. Since the HAN component is the most thermally sensitive constituent in the propellants, the presence of the second component has little or no influence on the start of decomposition, and the use of the nitrate salt of a primary, secondary, or tertiary amine should not affect the data obtained. HAN decomposes quite slowly during storage, albeit this process is accelerated by the presence of heavy metal ions (Klein 1976; Klein 1983; Klein 1984).

The decomposition of HAN is initiated by disproportionation which results in production of the unstable intermediate dihydroxylamine, $\text{NH}(\text{OH})_2$. Ammonium nitrate and nitric acid are also formed.



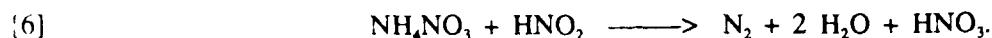
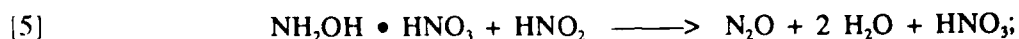
In the resultant acidic medium, the dihydroxylamine reacts producing nitrous oxide and water.



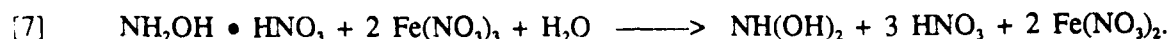
A secondary reaction involves the disproportionation of dihydroxylamine to HAN and nitrous acid.



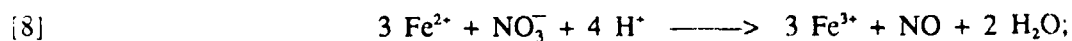
The nitrous acid is able to react with HAN, ammonium nitrate or organic ammonium salts. Nitrous oxide is formed with HAN and nitrogen with ammonium nitrate:



The formation of dihydroxylamine is encouraged by the presence of specific metal ions such as Fe and Cu. These metal ions are easily capable of undergoing valency changes, for example:



The reduced metal ions are, in turn, oxidized by oxidizing agents such as HNO_3 or O_2 :

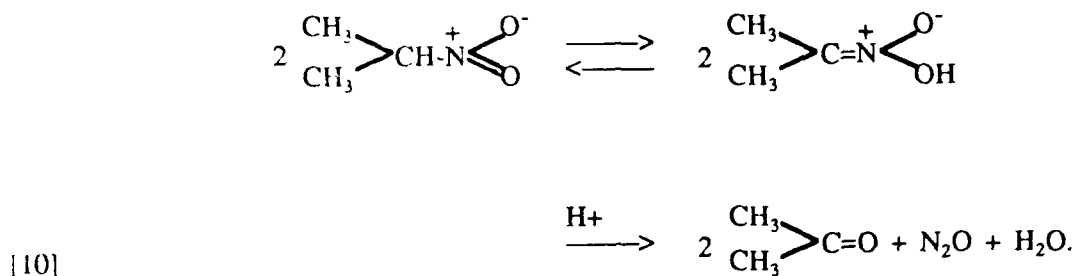


thereby recreating the species that oxidizes HAN in accordance with Equation [7]. Equations [8] and [9] basically describe the autocatalytic decomposition reactions observed in the propellants.

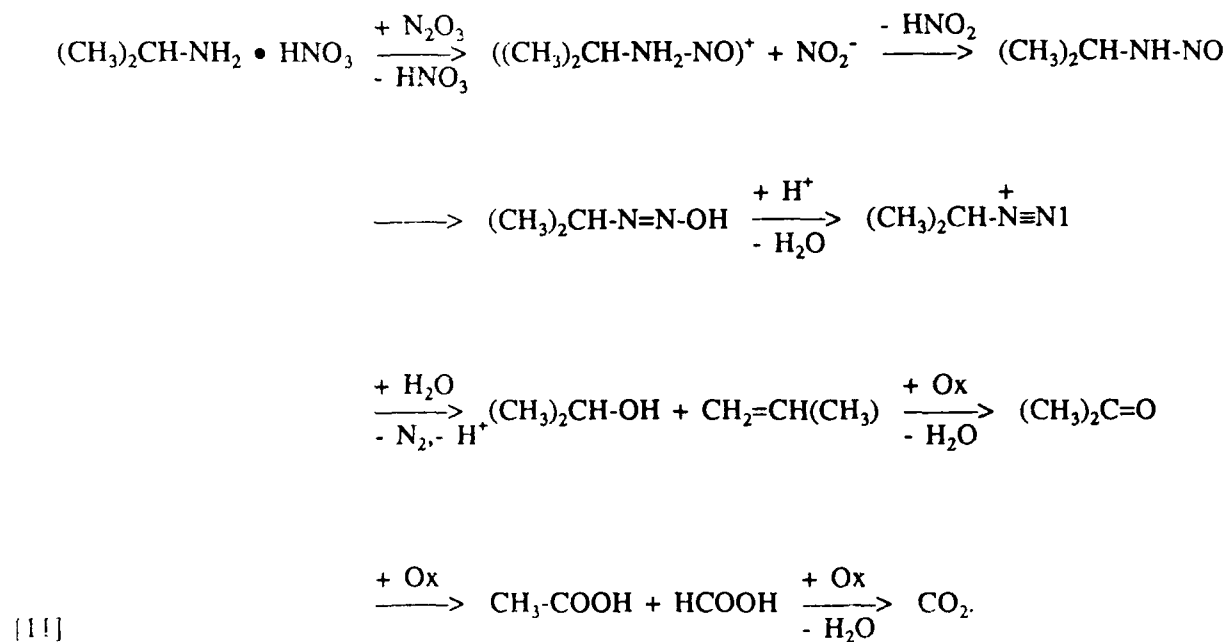
[EDITOR'S NOTE: Although the mechanism presented is plausible, it is, by no means, the only plausible reaction scheme that accounts for the thermal decomposition of HAN and the enhancement by transition metal ions of such decomposition.]

The possibilities of finding stabilizers for liquid propellants containing HAN or of binding the metal ion impurities through the formation of stable complexes, for example, are limited. The stability of metal complexes is reduced by the naturally acidic propellant mixture ($\text{pH} \approx 2.5$), and a new reaction would probably be required for each of the unwanted elements. Such coordination complexes would have to be extremely stable relative to the complex ions that already exist by reaction with the propellant ingredients, and it would appear that autocatalytic decomposition would be minimized primarily by maintaining a very high degree of purity.

The primary amino group, represented by isopropylammium nitrate, IPAN, can be oxidized to a nitro group. Following aci-nitroalkane degradation (Nef reaction), acetone is formed. Nitrous oxide, N_2O , is generated as a by-product.

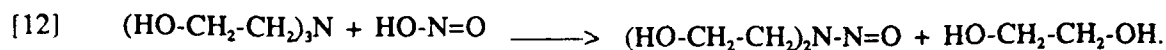


The primary amino group is also diazotized by reaction with nitrous acid and, in addition to nitrogen, the formation of carbon dioxide, isopropanol, acetic acid, and acetone is observed.

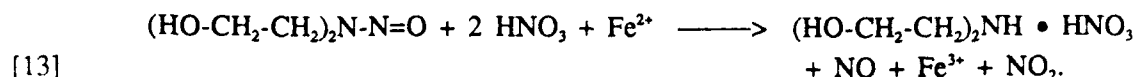


In parallel with these reactions, ω -oxidation of the amine is also conceivable.

No diazotization is possible in the case of the tertiary ammonium nitrates present in such propellants as LGP1776, LGP1845, and others. With such compounds, however, dealkylation via nitrous acid takes place with the formation of N-nitrosamines (Wegler 1936; Wegler 1937; Jones 1932). Aldehydes, ketones, or alcohols are produced from the separated alkyl residue (Smith 1967).

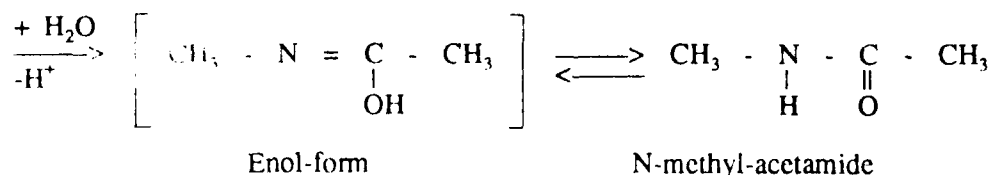
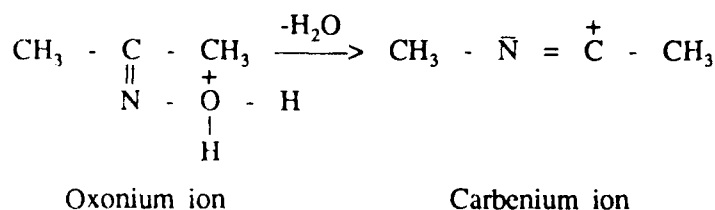
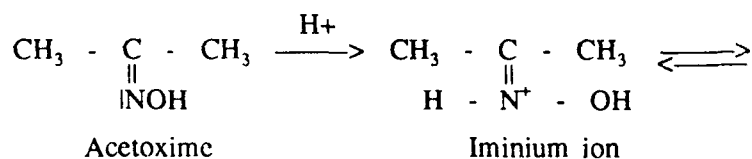


When metal ions such as Cu^{2+} or Fe^{2+} are present, the nitrosamines break down into secondary amine nitrates and nitrogen oxides (Lehmstedt 1927).



In addition, tertiary amines are subject to oxidation of the alkyl groups (ω -oxidation) and hydrolytic splitting. In this way, corresponding primary and secondary amine derivatives are produced from the less active tertiary amines, together with a large number of their reaction products (Price 1947; Fleury 1949; Hein 1963), ultimately resulting in the final products NO , N_2 and CO_2 .

Although the HAN-containing propellants are made up of relatively simple compounds, the production of a large number of degradation products can be demonstrated. In the presence of HAN, the corresponding oximes are formed from aldehydes and ketones. These oximes undergo Beckmann rearrangement, producing, for example, N-substituted carboxylic acid amides from ketoximes. By acid catalyzed hydrolysis, these amides then split up into amines and carboxylic acids.



Formation of larger quantities of the products described is only observed under unusual conditions. If combustion takes place, however, these intermediate products can influence burning behavior. The reaction schemes involving triethanolamine that have been discussed are summarized in Figure 1.

4. TEST METHODS TO DETERMINE THE THERMAL STABILITY OF LIQUID PROPELLANTS AT ELEVATED TEMPERATURES

The thermal stability testing of solid propellants has been standardized to a large extent and is usually set forth in propellant performance specifications. Parameters for stability assessment can be obtained, for example, from determination of weight loss, stabilizer decomposition, demonstration of the presence of decomposition products, pressure rise in sealed containers, or from the heat generated during thermal loading. In the case of liquid propellants, however, no such test specifications are available as yet. Test procedures analogous to those for solid propellants are problematic for the HAN-based liquid propellants, in part because of the vapor pressure of volatile components. During long-term storage, continuous evaporation of the volatile components takes place, producing a compositionally different material in place of the originally insensitive propellant. In some cases, this new material is unstable and is sensitive to manipulation. For this reason, test procedures must be employed that prevent partial evaporation of substances from the liquid during the simulation of aging processes. It follows that the test samples must be contained in an hermetically sealed system capable of withstanding the pressure developed during the storage period. All test methods in which this problem is not properly addressed will produce inaccurate and misleading results.

One method for assessing propellant storability is to subject samples to a simulated aging process at elevated temperature. The temperature chosen is usually higher than the maximum safe storage temperature specified in order to enhance decomposition and thus shorten the duration of the storage stability tests. Samples must be stored at this elevated temperature in sealed containers in order to prevent evaporation of water or other volatile components from the mixture. It was the aim of our work to develop processes for chemical stability testing in which long term storage of liquid propellants in closed systems could be carried out without undue risk.

[EDITOR'S NOTE: The validity of the concept of accelerated aging is subject to some question. The technique is valid only if it can be shown that the decomposition mechanism at the elevated temperature is the same as that observed at normal storage temperatures in which case reaction

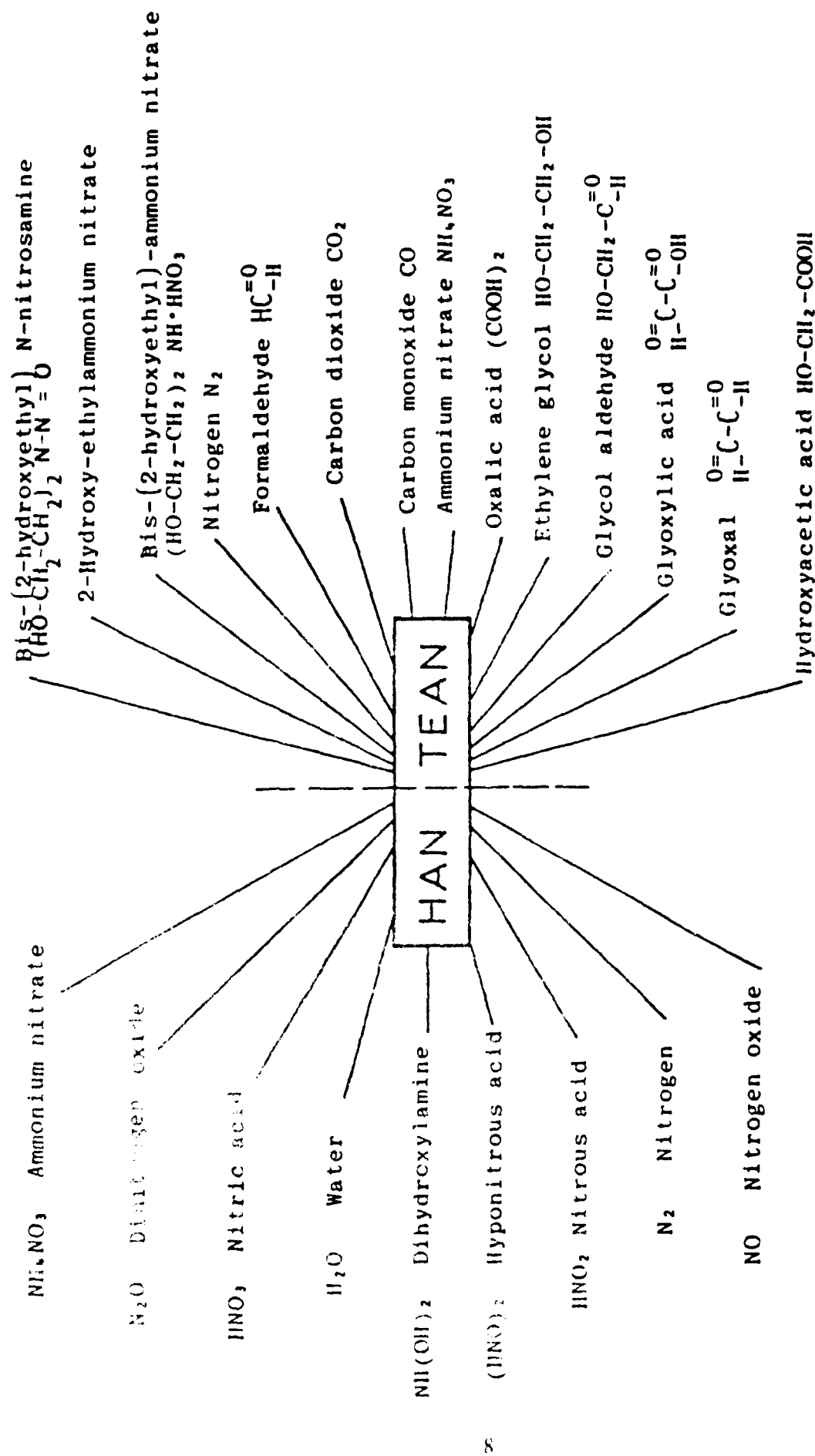


Figure 1. The Decomposition Products of the Liquid Propellant LGP1846.

acceleration associated with increased temperature applies. If, on the other hand, new reactions or a change in reaction kinetics appears at the elevated temperature, the data obtained may not be extrapolated. The validity of accelerated aging of the HAN-based liquid propellants has not yet been demonstrated.]

4.1 Storage in Sealed Glass Ampoules. The simplest accelerated aging test used involved sample storage in sealed glass ampoules. It is assumed that decomposition of the sample generates gaseous products and the time to ampoule bursting is taken as the stability test parameter. This test was used to assess the influence of variables such as the type and concentration of metal ions, pH, and stabilizers on the stability of the propellant. The test was also used to rapidly assess the suitability of various materials that would be in contact with propellant samples in other, more elaborate test procedures.

We found that glass ampoules of 5-cm³ capacity and having walls 0.6 mm thick were suitable as containers. The best were high quality medical ampoules, commercially available and manufactured on an industrial scale. The glass reacts with neither the propellants nor the various materials used in stability tests under the test conditions employed. The filled ampoules were closed by melting (flame sealing). The formation of propellant decomposition gases caused the pressure in the ampoules to rise gradually until they burst at approximately 10 bar. At first glance, the process just described may seem somewhat approximate, but if a number of conditions such as consistency of initial sample weight (0.7 g), the use of ampoules from the same lot, and care in maintaining cleanliness during sample preparation are strictly observed, replicate tests showed satisfactory agreement. At no point did sample-to-sample data variation exceed 20%, and the data trends obtained were readily interpretable. As example, the time to bursting of the ampoules containing LGP1846 plus 10 ppm iron ions was 21 days and compares with 86 days for pure propellant.

Premature bursting of the ampoules was a result of improper flame sealing. Slight deviations in wall thickness, which are unavoidable because of the industrial production methods used, had no noticeable influence on the results. It was possible to store up to 25 samples simultaneously at 90° C in a metal block thermostat. Assessment of bursting time took place at intervals of 24 hours. Each measurement reported is an average of five replicate tests. Although it would have been more desirable for statistical reasons, we nevertheless had to abandon employing a larger number of replicate reference samples for economic reasons. Only when a number of "exceptional cases" occurred did we have to repeat the measurement series.

A modification of this simple method for propellant testing consists of storing the samples in the heating block thermostats for predetermined periods of time such as 5, 10, or 15 days. Storage is then discontinued, and the samples are cooled in liquid nitrogen, opened, and their components analyzed. This procedure permits determination of the extent of decomposition as a function of storage duration.

The use of glass ampoules for screening tests and for comprehensive test programs was preferable to the more elaborate test methods that will be described subsequently. The following advantages were found:

- (1) Ampoule sealing posed no problem.
- (2) No complicated measuring equipment is required.
- (3) The samples are simple to handle.
- (4) The apparatus required is relatively economical.
- (5) Measurement accuracy is increased because a large number of replicate trials can be run.

In contrast, the following disadvantages should not be overlooked:

- (1) Pressure development cannot be controlled.
- (2) Pressure-time histories are not obtained, and thus comparisons with data obtained by chemical analysis are not possible.
- (3) Glass fragments and propellant residues are produced when the ampoules burst, in addition to which oxides of nitrogen are released.

4.2 Storage in Glass Containers With Pressure Sensors. During the aging of liquid propellants at elevated temperature, gases are produced. In a closed system, these decomposition products cause an increase in pressure which can be measured continuously with an appropriate pressure sensor. This method has the advantage that changes in the test sample can be continuously recorded as a function of time. Tests are discontinued and the sample residues subjected to analysis when a predetermined pressure is obtained. The time to the point when a specific pressure is reached is taken as a measurement of the relative stability of the propellant.

Glass containers with an exterior diameter of 12 mm, a length of 50 mm, and a wall thickness of 1.5 mm, having a volume of 2.9 cm³, were to be used. The containers were fitted with screwcaps (German standard GL 14 thread in accordance with DIN 168) and can withstand an

internal pressure of at least 30 bar. Pressure sensors would be set into a hole drilled through the sealing cap. Prior to selection of a final design, it was first necessary to make sure that material components of the test apparatus exerted no influence on the storage life of propellant samples.

4.2.1 Selection of Materials for the Construction of the Test Apparatus. Preliminary trials with various pressure sensors (Sensotec, Inc.) had shown that the surfaces of the sensor cases exhibited corrosion after exposure to HAN-based propellant at 90° C over a period of several months. Apart from water, hydroxylamine and nitric acid can also appear in the gas phase during the storage of propellants containing HAN at raised temperature, and, indeed, these substances were found via potentiometric titration in the vapor of LGP1846. Consequently, we first tested the interactions between metals, alloys, and polymers on LGP1846.

The test procedure described in Section 4.1 was used. Candidate materials and propellant were placed in ampoules which were then sealed and stored at elevated temperature. Since these stability tests involved a large number of materials that were not part of the container design screening process, complete results will be presented in subsequent sections, and only those results directly related to the apparatus design will be discussed at this point.

4.2.2 Metals and Alloys. Type 17-4PH stainless steel (German Standard No. 1.4542), from which the casing of the Sensotec pressure sensor is made, reacts with propellant LGP1846. The lifetime of the propellant sample is shortened to 23% of its original value. We made no attempt to passivate the stainless steels against LGP1846 at the ICT, although experience in this area has been obtained at the BRL (Klein 1987). Since long-term storage tests on LGP1846, in contact with gold, show no reduction in storage life of the propellant, the pressure transducers were galvanically gold-plated. Preliminary coating was with Au/Co alloy followed by a second coat of pure gold. The gold plating had a thickness of approximately 40 μm . In order to protect the parts not intended for gold plating, 30 cm long, radiation cross-linked, heat-shrinkable PVC tubing was drawn over the pressure transducers and their connecting cables prior to the galvanization process and subsequently removed. The plating integrity of each sensor was tested prior to use.

4.2.3 Plastomers and Elastomers. The materials used for sealing the pressure sensors must be selected with the same care as those for the pressure sensors themselves. The sealing materials must display high chemical resistance to the propellants, both in the liquid and gas phase, as well as to the decomposition products of the propellants. In addition, the sealing materials used may not influence the chemical stability or storage lifetime of the propellants. A total of 10 different

plastomers and elastomers were screened by tests in glass ampoules in order to select suitable sealing materials. The tests showed that only polytetrafluoroethylene PTFE - PT 950, PTFE-TFM, Teflon-PFA, and polytrifluorochloroethylene (PCTFE) are suitable. With these materials, the storage life of the samples was the same as that of the pure propellants. In addition to their chemical stability and compatibility with the liquid propellants, selection criteria for materials used in sealing the glass pressure containers also include their permeability to gases and their viscous flow behavior.

4.2.4 The Permeation of Gases Through Polymeric Substances. All polymers are permeable to gases to some extent. A planar membrane of thickness d and surface A exposed to a pressure difference Δp across it exhibits a gas flow Q from one side to the other. This transport process is called permeation, and if Δp is not too large, the process may be described by the linear relation (Lacey and Loeb 1972):

$$Q = P(A/d) \cdot \Delta p, \quad (1)$$

where P is a constant, the permeability or permeation coefficient. The quantity P is dependent on both the nature of the gas/membrane system and temperature. P is an exponential function of temperature:

$$P = P_0 \exp (-E/RT), \quad (2)$$

in which E is the activation energy, R the gas constant, T the temperature in Kelvin, and P_0 a constant. A straight line is obtained if $\ln P$ is plotted against $1/T$ and is used for determination of P at temperatures where experimental values are not available. The dimensions of the various quantities used for permeability calculations are as follows:

<u>Quantity</u>	<u>Unit</u>
Q	$m^3 \cdot s^{-1}$
A	m^2
d	m
Δp	Pa
T	K
P	$m^2 \cdot s^{-1} \cdot Pa^{-1}$

The permeation coefficient of sintered PTFE (Hostafion, Hoechst AG, FRG) for several gases is listed in Table 1, and the temperature dependence of the helium data is presented in Table 2. Comparable data for amorphous PCTFE (Voltalef, ATOCHEM, FRG) are listed in Table 3. The linearity of a $\ln P$ -vs.- $1/T$ plot of the Table 3 data can be seen in Figure 2.

Manufacturer-furnished permeability coefficients were used to calculate gas fluxes for flat sealing discs to be used in glass containers of the propellant test apparatus. A disc, 2 mm thick, with a 6-mm outer diameter and 4-mm inner diameter, was considered. Results for PTFE and PCTFE at 25° C and 90° C are given in Table 4. It can be seen from the Table that gas fluxes are highly dependent on the permeating gas. CO₂ permeates approximately 10 times faster than N₂ in TF 1740 and TFM 1700 while in Voltalef 300; this factor is about 30. Gas fluxes increase considerably with temperature in all cases although the difference between the two PTFE types is slight. Although not shown in the Table, the permeability of PTFE-TFM is 1.5 times lower than that of TF 1740. In all cases, PCTFE is less gas permeable than is PTFE.

The test protocol would call for sample storage at 90° C until a pressure of 4 bar is obtained. For PCTFE at 90° C and a 5 bar pressure differential, gas loss is approximately $1 \cdot 10^{-2}$ cm³/day. If we assume that, over a test period of 100 days, a pressure of 5 bar is present at the seal, the gas loss then amounts to approximately 1 cm³. Since the 2-cm³ test container holds about 10 ml of gas (NPT) at a pressure of 5 bar, a loss of 1 cm³ would mean an error of 10%. Since the pressure in the testing apparatus rises slowly and only reaches 4 bar toward the end of the test, the actual error is considerably less than that calculated. Nevertheless, the error assessment indicates that the pressure curves should flatten slightly toward the end of the test. Because pressure measurements are compared between samples rather than absolute, this error will tend to cancel.

4.2.5 Elasticity and Plasticity. Elastomers are especially suited for sealing the glass containers, and it is possible to incorporate 1 mm thick rubber washers between the screw cap and the pressure transducer. Maintenance of elastic properties (tension and compression behavior) during long-term storage at increased temperatures is a prerequisite for this modification. We therefore tested the compatibility of peroxidic cross-linked Viton (Viton GF) and of perfluorinated hydrocarbon (Kalrez 4079) with liquid propellant LGP1846 while testing the various sealing materials. The storage trials showed that the lifetime of the liquid propellant is considerably shortened by contact with the elastomers. Kalrez 4079 lowers storage life to 48%, and Viton GF lowers storage life to 25% of pure propellant. In addition, gas permeation is 80 times greater for Viton GF and 600 times greater for Kalrez 4079 than it is for PCTFE. Both elastomers, therefore,

Table 1. The Permeation Coefficient, P, of Sintered PTFE (Hostaflon) at Room Temperature in Accordance With German Standard DIN 53380.

Gas	P (cm ³ /day) per bar	
	TF 1740	TFM 1700
Air	100	80
O ₂	250	160
N ₂	80	60
CO ₂	700	450
He	2100	1700
Water Vapor	0.03	0.03

Table 2. Temperature Dependence of the Helium Permeation Coefficient, P, of PTFE (Hostaflon).

Temperature °C	P (cm ³ /day) per bar TF 1632
23	2400
35	3000
50	4100

Table 3. Temperature Dependence of the Permeation Coefficient, P, of Amorphous PCTFE (Vortalef 300) for a Number of Gases. Permeation Coefficient x 10¹⁰.

Temperature in °C	P (cm ³ /sec) per cm Hg					
	Gas					
	N ₂	O ₂	CO ₂	H ₂	H ₂ S	Water Vapor
0	-	0.07	0.35	3.20	-	-
25	0.05	0.40	1.40	9.80	-	1
50	0.30	1.40	2.40	24.0	0.35	10
75	0.91	5.70	15.0	-	2.0	28
100	-	-	-	-	-	100

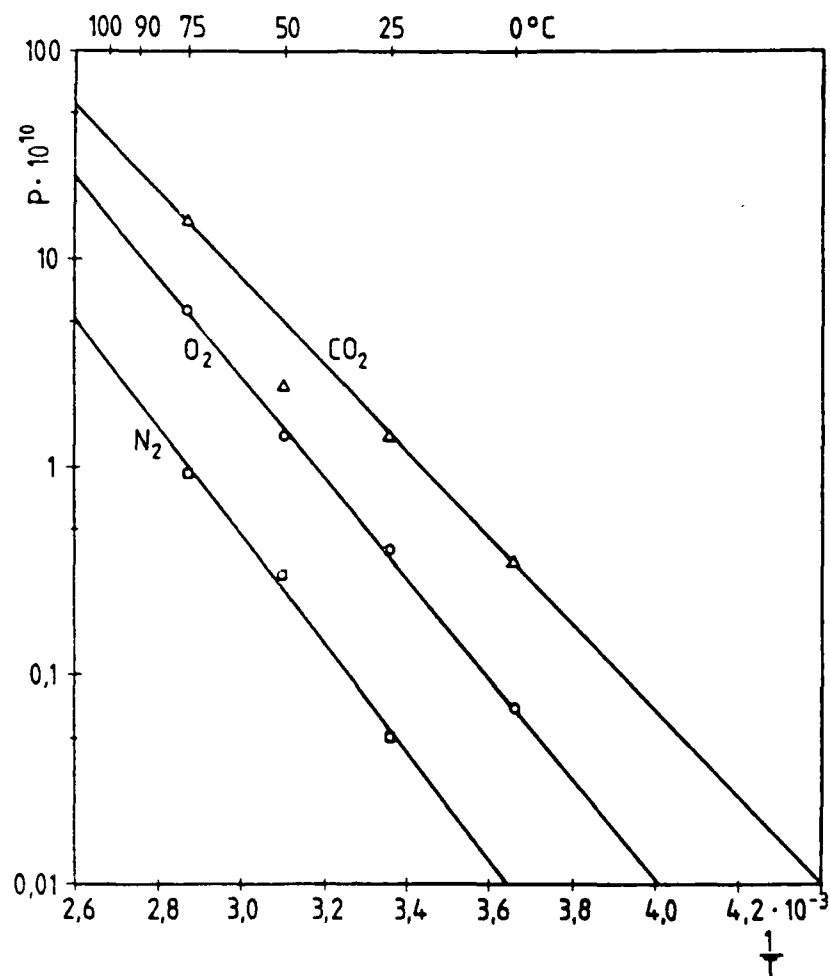


Figure 2. Temperature Dependence of the Permeation Coefficient, P, of PCTFE (Vultalef 300) for N₂, O₂, and CO₂. P in cm • mm/s • (cm Hg); T in K.

Table 4. Gas Fluxes, Q, Through PTFE and PCTFE at 25 and 90° C, Calculated for Flat Sealing Elements (r_o = 6 mm, r_i = 4 mm, d = 2 mm, A = 0.63 cm²).

Gas	Q (cm ³ /day) Δp = 5 bar					
	<u>PTFE (Hostaflon)</u>				<u>PCTFE</u>	
	TF 1740		TFM 1700		Vultalef 300	
	25° C	90° C	25° C	90° C	25° C	90° C
N ₂	1.25•10 ⁻²		9.5•10 ⁻³		5.1•10 ⁻⁵	2.0•10 ⁻³
O ₂	3.92•10 ⁻²		2.52•10 ⁻²		4.1•10 ⁻⁴	1.1•10 ⁻²
CO ₂	1.1•10 ⁻¹		7.1•10 ⁻²		1.4•10 ⁻³	2.7•10 ⁻²
He	3.83•10 ⁻¹	1.26				

are not suitable as sealing materials for the long-term testing apparatus. We considered using PTFE-coated Viton O-rings but the PTFE coating is a mere 0.4 mm thick. It can be seen from Section 4.2.4 that the use of 0.4 mm thick PTFE foil to seal glass containers for long-term storage tests is not possible due to its excessively high gas permeability.

Plastomers, especially PTFE, are subject to deformation under strain. Modified PTFE (TF 1740, TF 1700) deforms 1.5-2.5% at 25° C when subjected to 7 MPa for 24 hours. Comparable data for PCTFE is 1%. Generally, deformation under strain decreases as hardness increases, the PTFE samples exhibiting a Shore hardness of 55 to 60, whereas PCTFE (Voltalef 300) has hardness values in the 77-79 range. PCTFE was selected as the sealing material for the glass containers because it exhibits the highest Shore hardness, the lowest deformation under strain, and the smallest permeation coefficient.

The 1% stress-induced deformation of PCTFE caused difficulties to be encountered at times with sealing of the test apparatus. A part of the apparatus leaked during long-term storage, and pressure did not continue to rise. Attempts were made to increase the sealing efficiency of the test apparatus by using spring-loaded seals in place of plastomers.

As an alternative to the melamine resin screwcap for the glass container, we constructed a sealing device consisting of a tightening frame and a screw-mounted spring. The screw was operated by a milled head. However, the spring was found to be too weak, and we encountered problems in the housing of the spiral spring. We considered exchanging the coil spring for a bank of cup springs, since cup springs are suitable where a greater spring force is required over small lengths. The high cost of producing the tightening devices (60 separate units were needed), eliminated their use.

After selection of PCTFE as the most suitable sealing material, a special trial was carried out to test the tightness of glass containers with pressure sensors. A known quantity of gaseous nitrogen was produced by the reaction of standardized sodium nitrite solution with excess solid amidosulfonic acid in the sealed container. The amidosulfonic acid was held in a small glass crucible which could be moved remotely by a glass-encapsulated micromagnetic stirrer. We were thus able to produce the gas after the container had been tightly sealed. The glass container was kept at room temperature. Table 5 shows the pressure in the glass container, as measured by the pressure sensor, over a period of 36 days. Pressure was corrected according to the equation of state for ideal gases. Other corrections, such as the solubility of nitrogen in the aqueous solution

Table 5. Gas Pressure, P, in Glass Containers as a Function of Time, t; T_c = Measurement Temperature in °C.

$\frac{t}{\text{Days}}$	$\frac{T_c}{^\circ\text{C}}$	$\frac{P}{\text{bar}}$
0	22.0	2.05
1	21.0	2.01
2	20.0	2.00
3	20.0	2.01
4	20.0	2.00
7	21.5	2.05
8	21.5	2.08
9	21.3	2.06
10	20.5	2.03
11	19.0	2.01
13	19.5	2.00
14	20.4	2.00
15	19.3	1.98
16	18.9	1.96
17	20.5	1.97
18	20.2	1.98
19	20.0	1.99
20	20.7	2.00
24	19.9	1.95
25	19.8	1.95
29	21.0	1.98
30	22.8	2.02
31	23.0	2.04
32	22.8	2.07
33	19.3	2.04
35	19.0	2.02
36	19.9	2.03

and the partial pressure of water vapor were not taken into account. The maximum difference in pressure measured was about 6-7% although a systematic, time-dependent drop in pressure was not observed. Based on these measurements, the thickness of the PCTFE sealing element was reduced from 2 to 1 mm, and a tension wrench was used to tighten the plastic screw caps.

Figure 3 gives details of the measuring equipment. The pressure sensors used were Sensotec subminiature pressure transducers model 81G (manufactured by Sensotec Inc., and supplied by H. Burster, FRG) with a foil-type strain gauge and full bridge. The transducer case is made of type 17-4PH stainless steel (German standard, Mat. No. 1.4542). To protect against corrosion, the casings received a thick gold plating before final calibration. Pressure was recorded using a UPM

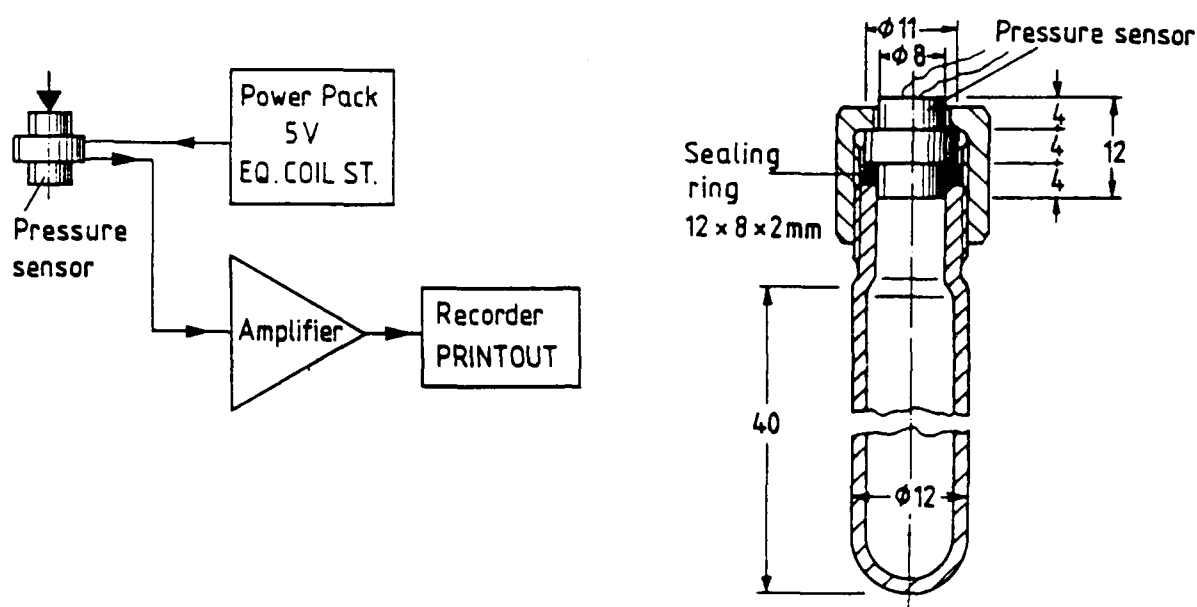


Figure 3. Test Arrangement for Liquid Propellant Pressure Measurements (all dimensions are in millimeters).

60 multipoint measurement unit manufactured by Hottinger Baldwin Messtechnik (FGR). This processor/recorder is designed to accommodate a maximum of 60 measurement leads and is equipped with integrated measuring amplifiers, A-to-D converters, microprocessor, V 24 computer interface, and paper strip printer. The gauges are capable of measuring pressures to a maximum of 5 bar and were calibrated with an automatic pressure calibration apparatus, type EPK 20, manufactured by Promotek.

The weight of the samples used was precisely 1 gram. For safety reasons, we do not recommend larger sample weights. The glass containers with the samples and the attached pressure transducers were maintained isothermally by immersion in a thermostatically controlled heating block. This prevents change in propellant concentration by evaporation of water and condensation at cooler parts of the containers. For reasons of safety, a pressure of 4 bar was fixed as the maximum pressure limit. The data recorded are pressure-time diagrams, thus clearly showing the progress of decomposition.

Continuous pressure measurements during the aging of liquid propellants in pressure containers present the following advantages:

- (1) Pressure-time histories are obtained.
- (2) Both the control of pressure and timely recognition of critical pressure values are possible.
- (3) Comparison of the chemical composition of the sample residue and the quantity of decomposition gases is possible.
- (4) At a pre-specified pressure, gas analyses can be carried out with a mass spectrometer, for example.

However, this measurement technique has the following disadvantages:

- (1) Spontaneous decomposition of the propellant could destroy the sensor.
- (2) Sophisticated electronic equipment is required.
- (3) The expense of the measuring apparatus and pressure sensors sets a limit to the number of trials running in parallel.

4.3 Storage in Glass Ampoules with Strain-Gauges. The test arrangement described in Section 4.2 subjects the pressure sensor and the seals to elevated temperature and an acidic atmosphere for the duration of the storage period. As a possible alternative to these very severe conditions, attempts were made to measure pressure rise in sealed, thin-walled (< 0.5 mm) ampoules using strain gauges attached to the outside wall of the ampoule since the pressure generated by the gaseous decomposition products causes transverse and longitudinal expansion of the ampoule walls. The advantage of this technique is found in the fact that the strain-gauge pressure sensor does not come into contact with the liquid tested and that the ampoule is flame-sealed.

Test measurements in half-bridge circuits with temperature compensation were carried out in which an active strip was attached to the flame-sealed ampoule and a compensation strip onto an empty, open test container. A total of 10 simultaneous measurements can be made with the UPM 60 multisite measurement unit used in this way. Additional tests using half-bridge circuitry without temperature compensation were carried out in which a fixed resistance was used in place of the compensation strain gauge. The measurements using either test arrangement showed that the strain gauge sensitive to longitudinal force exhibited a low rate of expansion, but the gauge sensitive to transverse forces recorded relatively high expansion values of $12.5 \mu\text{m}/\text{bar}$. Figure 4 shows the pressure curves obtained. Although the technique is feasible, it has the disadvantage that each glass ampoule had to be individually calibrated and temperature corrected. We, therefore, preferred the method described in Section 4.2.

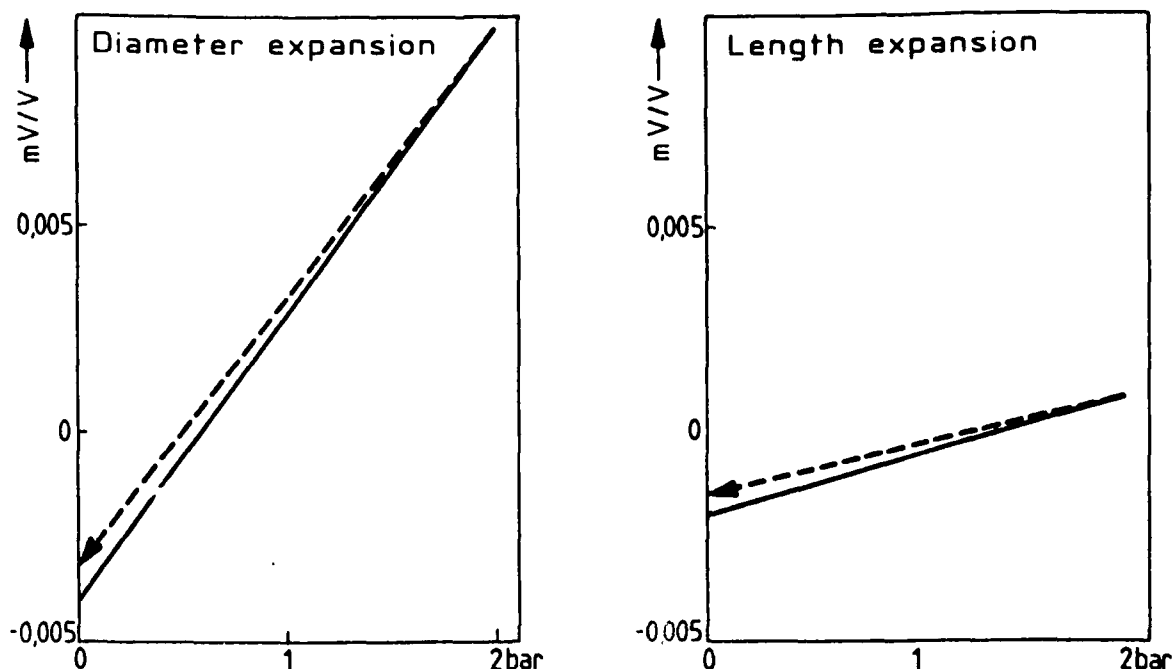


Figure 4. Measurement of Longitudinal and Transverse Expansion as a Function of Internal Pressure Using Strain Gauges on Glass Ampoules.

5. QUANTITATIVE PROPELLANT ANALYSES

5.1 Propellant Composition. The composition of a number of liquid propellants is given in Table 6. All of the propellants contain hydroxylammonium nitrate and the nitrate salt of an organic amine. The amine that was originally selected was isopropylammonium nitrate, IPAN, but it was then found that IPAN produced poor combustion kinetics (Klein 1987). It was eventually replaced by triethanolammonium nitrate, TEAN, and the propellants generally used at present are LGP1845 and LGP1846. Mixtures of HAN, the amine nitrate, and water are liquids. In view of its relatively low water content of approximately 20% by weight, the liquid propellant mixture should be considered salt melts rather than aqueous solutions. Ammonium nitrate, AN, is not listed in Table 6. It either occurs as an impurity in the components or is produced as a decomposition product. Even small quantities of AN are claimed to raise the freezing point of the propellant (Klein 1987).

5.2 Methods of Analysis. Separation and quantitative determination of the propellant components by gas chromatography appears to be possible. For this purpose, the amines should first be liberated in an alkaline preparatory column. However, it is questionable whether hydroxylamine would survive the separation process without decomposition. No examples are given in the literature, and we did not carry out experiments of our own.

Table 6. Composition of Liquid Propellants.

Code Name	FUEL		HAN, wt. %	Water, wt. %	Oxygen Balance, %	Impetus, l/g	Flame Temp., K
	Symbol	wt. %					
LGP1776	TMAN	19.3	60.8	19.9	0.03	960.7	2600
LGP1781	EOAN	32.5	50.3	17.2	- 0.0	929.6	2560
LGP1812	TEN	13.6	67.5	18.9	- 0.04	959.8	2670
LGP1814	TEN	13.2	65.3	21.5	- 0.1	924.7	2500
LGP1835	TEN	11.8	68.4	19.8	+ 3.25	885.7	2410
LGP1845	TEAN	20.0	63.2	16.8	- 0.05	982.3	2730
LGP1846	TEAN	19.2	60.8	20.0	- 0.01	934.5	2570
LGP1848	TEAN	14.5	66.3	19.2	+ 6.78	820.7	2260

TMAN ... Trimethylammonium nitrate	$(\text{CH}_3)_3\text{N}\cdot\text{HNO}_3$
EOAN ... Ethanol ammonium nitrate	$\text{HO CH}_2\text{CH}_2\text{NH}_2\cdot\text{HNO}_3$
TEN ... Triethylammonium nitrate	$(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{HNO}_3$
TEAN ... Triethanolammonium nitrate	$(\text{HO CH}_2\text{CH}_2)_3\text{N}\cdot\text{HNO}_3$

Ion chromatography is, without doubt, a chemically conservative separation process that has been developed for analyses in the parts per million range. The required sample volume is approximately 100 μl (0.1 ml), and the individual ions are usually detected and quantitatively determined by conductivity measurements. The accuracy needed for analytical determination of major sample components, however, is not obtained.

For the determinations needed in this study, we chose the methods of volumetric analysis. These are generally accurate to better than 1%, and frequently several analytical procedures are available for one component (e.g., analysis via neutralization, oxidation, and/or precipitation), which considerably improves reliability. Reference solutions, which are difficult to prepare and require standardization by volumetric analysis, are not necessary. Propellant analysis requires that a number of compounds, generally three, be titrated sequentially. A simple apparatus using chemical indicators is not adequate, and potentiometric determination of the equivalence point is the most suitable method (Kraft and Fischer 1972). The use of automatically recording titration equipment saves time. Since the visual evaluation of titration curves is difficult or impossible where the points of inflection associated with equivalence points are weak, the use of microprocessor-assisted titration equipment is not only recommended but necessary (Henze and Neeb 1986).

5.3 The Titroprozessor 636. The Metrohm Model 636 Titroprozessor, Program Group P 100, is an analog/digital measurement and titration apparatus for general potentiometric application. The unit is equipped with a 16-bit microprocessor which processes and evaluates signals, controls peripheral equipment, and produces the output data. Data evaluation programs used to calculate equivalence points from titration curves are based on methods obtained from the literature (Kraft and Fischer 1972), and, where necessary, the manufacturer has modified evaluation methods (Firmenschrift der Metrohm). The manufacturer states that the apparatus is capable of detecting equivalence points which cannot be recognized visually as points of inflection in the titration curves. Differences between points of inflection and equivalence points that would produce erroneous results are corrected, for the most part, in the system. Examples supplied by the manufacturer show that simultaneous determination is still possible where equivalence points differ by 2.5 to 3 pH units. This corresponds to differences of 300 to 1,000 in K_a values and appears to be the performance limit of the Titroprozessor 636 for simultaneous determination of weak acids or bases.

Figure 5 shows the Titroprozessor 636 as set up for propellant analysis. The apparatus incorporates two motor-driven piston burettes of the Dosimat 635 type and a motor-driven piston burette of the Dosimat 665 type with integrated microprocessor, sample container with magnetic

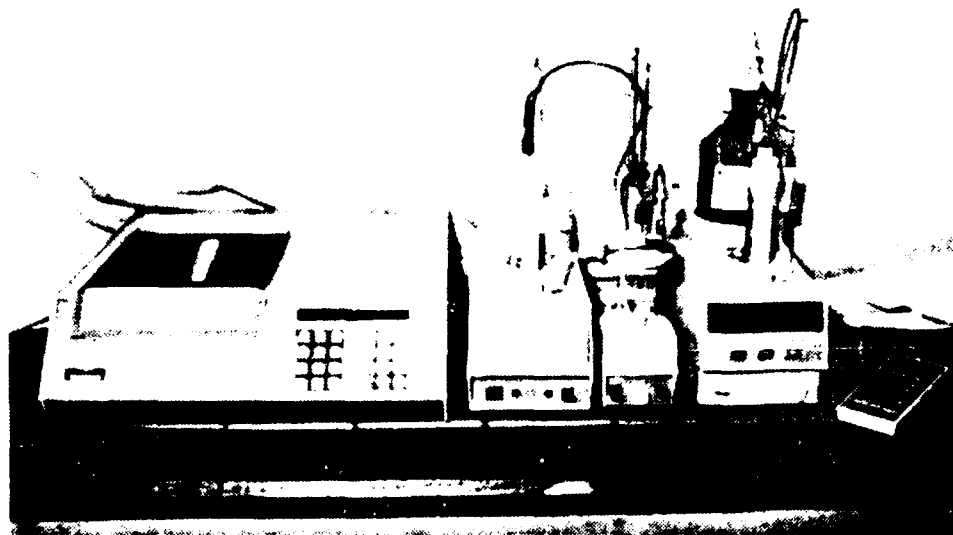


Figure 5. The Metrohm Titroprozessor 636 as Used for Propellant Analysis.

stirrer, and indicator electrode holder. The three piston burettes allow freely selectable addition of titrant such as 0.5 N or 0.05 N KOH, or 1 N NH_4NO_3 , and the addition of auxiliary reagents such as acetone or formaldehyde solutions. A combined pH glass electrode ("single-rod glass electrode") with a U glass membrane is used. The Titrator is controlled by cards that establish operation and calculation modes and are programmed by "rubbing on" square black code markings.

Titration can be carried out in any of three operating modes:

- (1) Dynamic titration with variable volume steps; a small number of measurement points are taken if the rate of change of the output signal is small and many measurement points are recorded at high rates of change.
- (2) Dynamic titration with variable volume steps up to a preselected final point; the addition of reagent is interrupted when a preselected final point or potential is reached.
- (3) Monotonic titration with constant volume steps; data collection only when low rates of change in output signal is expected

5.4 Acid/Base Titration and pK Values. All of the propellant components given in Table 6 are the salts of a relatively strong acid (nitric) and organic or inorganic amines, all of which are weak bases. In water, these salts produce acidic solutions with pH values below 7. The salts can therefore be neutralized with a strong base such as potassium hydroxide causing the weak bases to be liberated from their salts. Even the strongest of these bases such as ammonia and the primary organic amines, produce equivalence points that are well into the alkaline range with pH above 10. As a result, end points overlap and can then no longer be determined with color indicators such as phenolphthalein.

Concentrations of the individual ions can be determined in mixtures of different acids or bases by sequential titration if the end point potentials are sufficiently different from one another. These potentials depend on the dissociation constants K_A and K_B of the relevant acids or bases. pK , a value analogous to pH and defined as: $pK_A = -\log K_A$ or $pK_B = -\log K_B$ is sometimes used. The equation:

$$pH = pK_A - \log(C_{acid}/C_{salt}) \quad (3)$$

describes the relationship between the pK value of a weak acid or base in aqueous solution and the measured pH value of its solution where C_{acid} and C_{salt} are the concentrations of an acid and its salt, respectively, and are obtained either from initial weight or analysis. Activity coefficients are generally negligible because of the low concentrations involved. When the concentrations of acid and salt are equal, the logarithmic term in Equation (3) becomes zero. In such a case, $pH = pK_A$ or pK_B . The values of pK can then be measured via potentiometric titration since the pK value is equal to the pH value measured at half neutralization. The pK_A and pK_B values are related as:

$$pK_w = pK_A + pK_B, \quad (4)$$

the value of pK_w being the negative logarithm of the ion product of water which, at 20 °C is $0.68 \cdot 10^{-14} \text{ mol}^2 \cdot \text{dm}^{-6}$; $pK_w = 14.17$.

The values for K_A , pK_A , and pK_B have been assembled in Table 7 for the most important propellant components. The values were determined by titration of the nitrate salts of the amines with potassium hydroxide. The pK_A values are obtained as the pH values measured at the mid-point of the titration curve (Firmenschrift der Metrohm AG p. 100). The combined glass electrode used in the measurement was calibrated by comparison with two buffer solutions of known pH

Table 7. Dissociation Constants K_A as Well as Relevant pK_A and pK_B Values of Several Propellant Components in Aqueous Solution at 20° C.

No.	Propellant Components	K_A	pK_A	pK_B	pK_B (Literature Values)	Reference
		$\text{mol}^2 \text{ dm}^{-6}$				
1	Hydroxylammonium nitrate (HAN) + formaldehyde (formaldoxime)	$0.245 \cdot 10^{-1}$	1.61	12.56	-	-
2	Hydroxylammonium nitrate (HAN) + acetone (acetoxime)	$0.191 \cdot 10^{-1}$	1.72	12.45	12.19	18
3	Ammonium nitrate (AN) + formaldehyde (hexamethylene tetramine)	$0.141 \cdot 10^{-5}$	5.85	8.32	8.85 9.1	19 17
4	Hydroxylammonium nitrate (HAN)	$0.733 \cdot 10^{-6}$	6.135	8.035	8.03	18
5	Triethanolammonium nitrate (TEAN)	$0.112 \cdot 10^{-7}$	7.95	6.22	6.23	18
6	Ammonium nitrate (AN)	$0.331 \cdot 10^{-9}$	9.48	4.69	4.75	18
7	Isopropylammonium nitrate (IPAN)	$0.138 \cdot 10^{-10}$	10.86	3.31	3.37	18

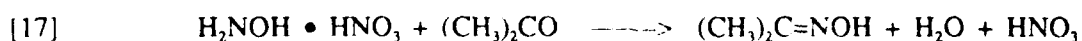
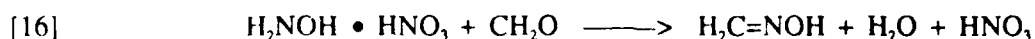
value (Firmenschrift der Metrohm AG p. 100). As far as possible, the same experimental conditions were used for pK_A determinations as were used subsequently for sample analyses (quantity, volume and temperature of the sample, normality of standard solutions, etc). pK_b and K_A values were calculated from the pK_A values. When available, pK_b values obtained from the literature are included in Table 7. The methods used to obtain these literature values are not known. In the case of hexamethylene tetramine, the two literature values differ considerably. Considering the uncertainties involved, the agreement between the experimentally determined and literature values is regarded as satisfactory. The salts are listed in order of decreasing acidity.

Simultaneous determination of a number of acids or bases usually requires that their dissociation constants differ substantially from one another. This difference should be at least 1,000 (Klein 1987; Poethke 1980), although the microprocessor-assisted titration apparatus makes it possible to detect weaker and more closely adjacent end points (Henze and Neeb 1986). The situation is made worse if one of the salts is present in much smaller quantity than the other, an AN impurity in HAN, for example. The equivalence point of the AN is then masked by HAN in the titration curves.

The measured acidity obtained from quantities of ammonium and hydroxylammonium salts can be increased through derivative formation, a procedure that generates nitric acid quantitatively from the salts. End points are thus shifted to lower pH values, and it becomes possible to determine propellant components simultaneously. Ammonium salts react with formaldehyde to form the very weak base, hexamethylene tetramine, and nitric acid:



The sample can be titrated with potassium hydroxide after the addition of formaldehyde using phenolphthalein as an end point indicator (Poethke 1980). The reaction is specific for ammonium salts and ammonia because organic amines do not react with formaldehyde under these conditions. Similarly, hydroxylammonium salts react with aldehydes and ketones forming aldoximes and ketoximes respectively. For example, formaldoxime or acetoxime and nitric acid is obtained from hydroxylammonium nitrate with formaldehyde or acetone:



Separation in pK_A now permits analyses to proceed readily.

5.5 Propellant Analyses.

5.5.1 Propellants Containing a Primary Amine. In the case of a propellant containing the nitrate salt of a primary amine such as IPAN, Table 7 indicates that simultaneous titration of the components should be possible with a strong base without difficulty. This is confirmed by the titration curve shown in Figure 6a. The end point of HAN (1), the first component determined is clearly prominent as a point of inflection since the K_a values of HAN and IPAN differ by $5.3 \cdot 10^4$. The IPAN end point (2) is, however, difficult to recognize without additional processing owing to its high pH and lower concentration. Figure 6b, which is the first derivative of the Figure 6a curve, further clarifies this point. In Figure 6b, the end points appear as maxima or minima and the second equivalence point is recognizable as the crossing of the two, almost straight, lines. The accuracy obtained for the determination of IPAN should be less than that expected for HAN.

The addition of acetone to the HAN-IPAN mixture converts HAN to acetoxime and nitric acid, and the HAN end point is shifted to lower pH. The change in pH in the equivalence range is so large, in fact, that an indicator such as methyl red could be used for end point determination. As can be seen in Figure 7a and its first derivative, Figure 7b, the conversion of HAN to nitric acid separates the end points but does not change the shape or amplitude of the IPAN end point.

The presence of ammonium nitrate, AN, in a HAN-IPAN mixture requires production of two derivatives for detection and analysis. Both acetone and formaldehyde must be added with acetone added first since both HAN and AN will produce nitric acid upon reaction with formaldehyde. As seen in Table 7, the difference in K_a values for HAN and AN now becomes $1.4 \cdot 10^4$, and for AN and IPAN the difference becomes $1.0 \cdot 10^5$. Figures 8a and 8b demonstrate the technique used. The formation of acetoxime and hexamethylene tetramine permits the three components to be separated and determined. Since the quantity of AN is small in the sample (generally below 0.5 wt-%), the end point must be enlarged by adding a known quantity of ammonium nitrate prior to analysis. The actual AN content of the propellant is calculated as the difference in end points between two samples that have almost the same AN concentration and the accuracy attainable in such cases is only moderate. On the other hand, the substances are present only in low concentration, and the lower accuracy is adequate.

5.5.2 LGP1845 and LGP1846. The presence of free nitric acid in propellant mixtures is a matter of considerable interest. A simple pH measurement would be inadequate because the salts in the mixtures act as buffers. We therefore attempted to determine free nitric acid in the propellant

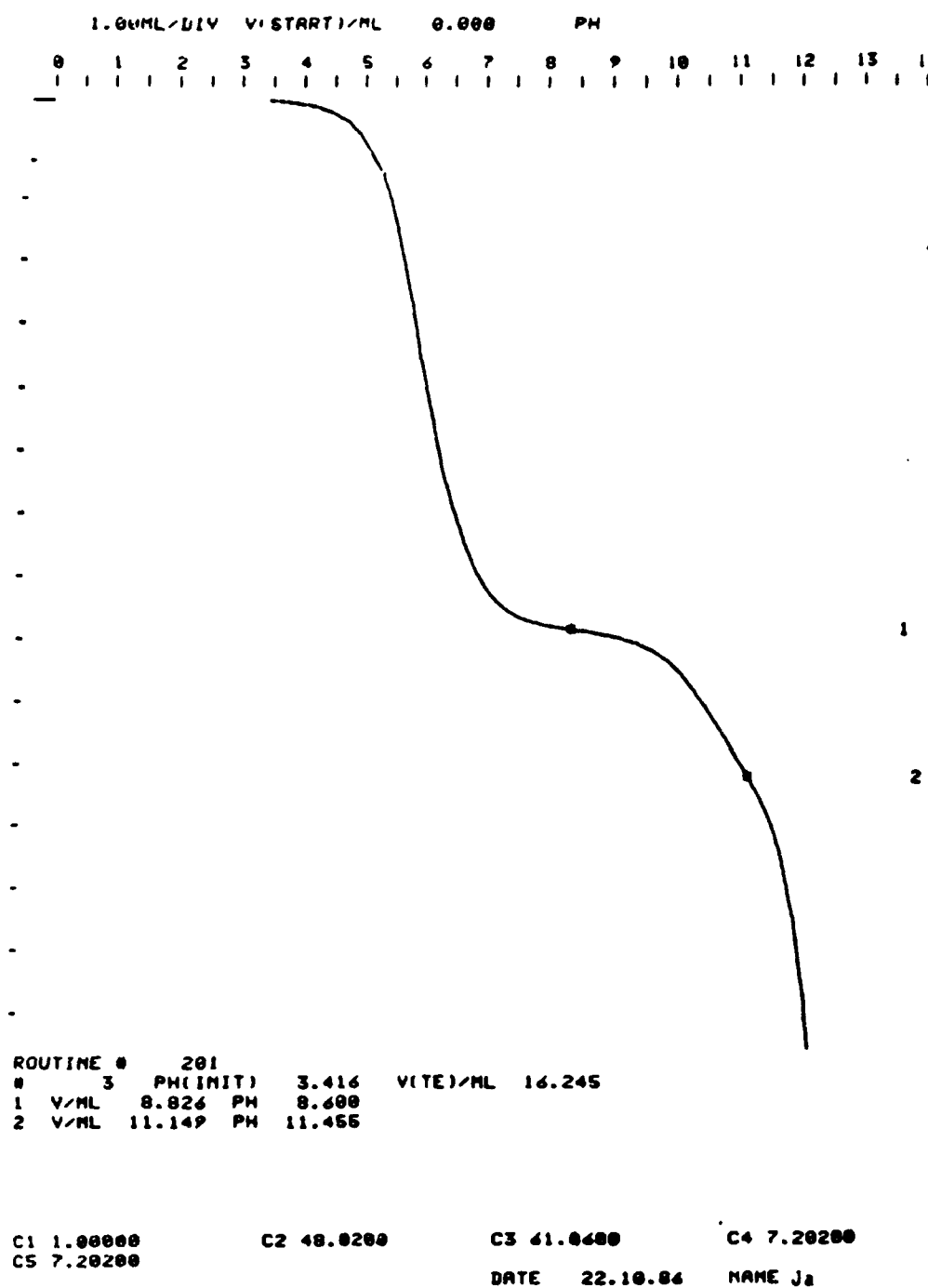


Figure 6a. Simultaneous Determination of HAN and IPAN by Titration.

by potentiometric titration with 0.05 N potassium hydroxide. Figure 9 shows the titration curve obtained. The point of inflection in the titration curve (1) is identified by the microprocessor as the equivalence point with a small but clearly seen maximum in the first derivative. The free nitric acid content was determined to be 0.31 wt.-%, a value which seems reasonable.

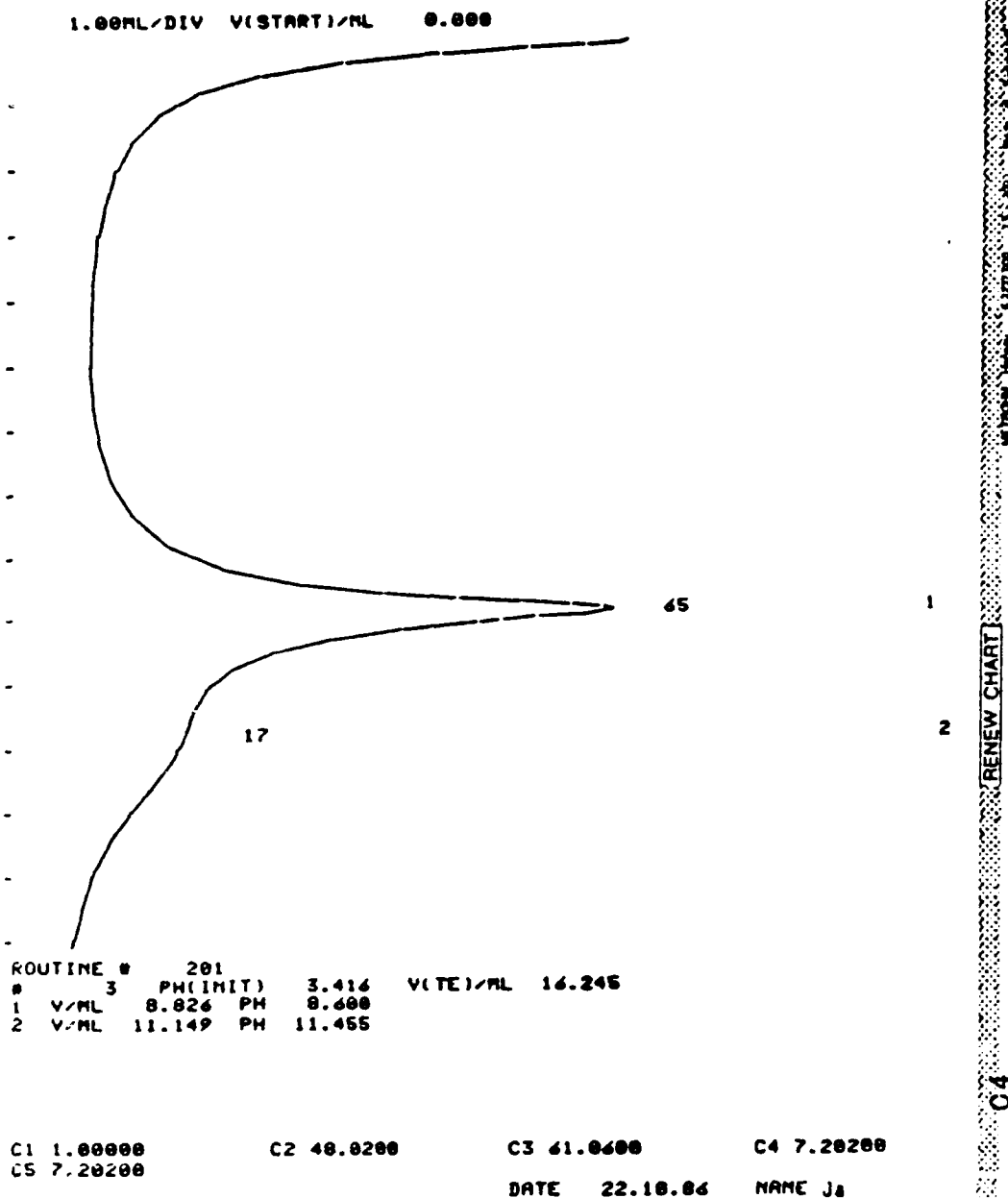


Figure 6b. Simultaneous Determination of HAN and IPAN by Titration: First Derivative of Titration Curve.

The separation of HAN and TEAN by simple titration is not possible since the difference in K_A values is only 65. After addition of acetone and the formation of acetoxime, the K_A difference is $10.6 \cdot 10^6$, and separation is readily obtained. The TEAN end point is more clearly indicated than was that of IPAN because end point separation is much greater, triethanolamine being a weaker base than isopropylamine. Typical titration curves obtained are shown in Figures 10a and 10b, the sharp maxima in Figure 10b confirming the large end point separation obtained.

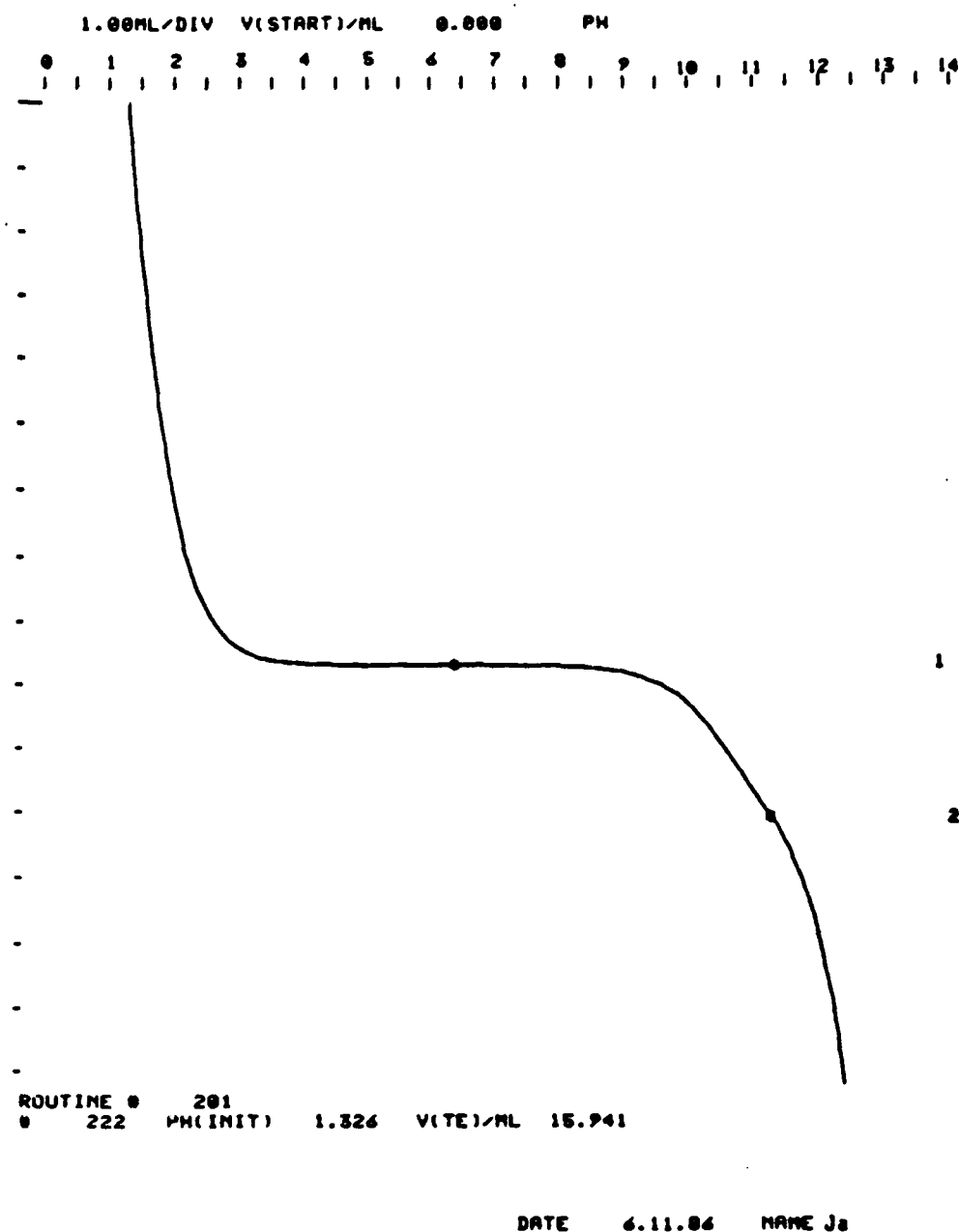
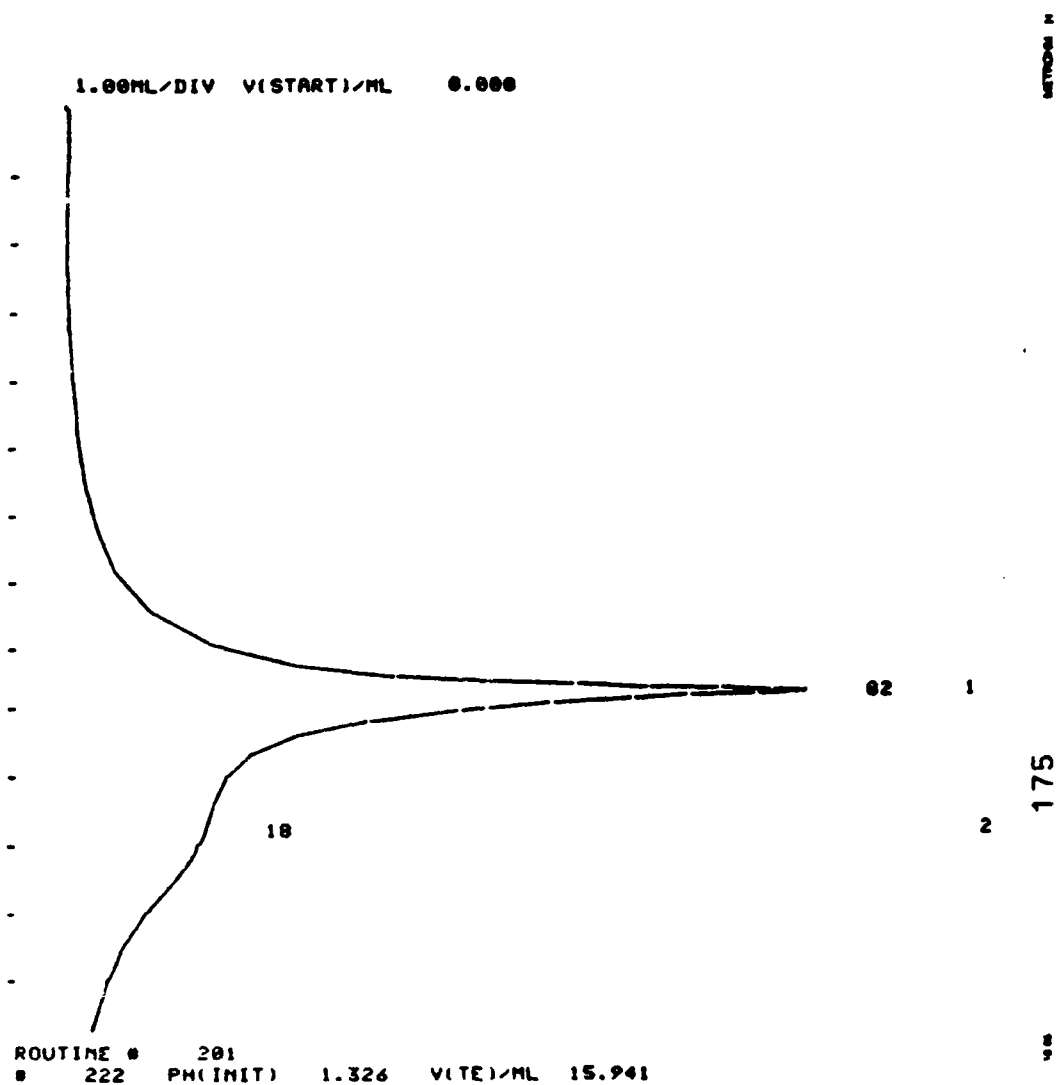


Figure 7a. Simultaneous Determination of HAN and IPAN by Titration After Formation of Acetoxime by Acetone Addition.

The simultaneous determination of AN in a HAN-TEAN mixture by titrimetry is not possible. The AN-TEAN K_A difference is 34 and increases to only $1.3 \cdot 10^2$ after reaction with formaldehyde. The inflection points obtained in the titration curves do not agree with the equivalence points, and



DATE 6.11.86 NAME JA

BUR.2 V/ML	20.0	ROUTINE #	201
TEMP/C	18.0	REAGENT	0.5 n KOH w&Br. Titrisol
KINET D	8.0	TITER	1.000
MPD VAR	8.0	ELECTRODES	2 kombinierte Glaselektrode Metrohm, geeicht
START V/ML	0.000	SAMPLE	712,8 mg NOS 365 + 10 ml Aceton
STOP PH	100.000		
STOP V/ML	20.000		
STOP # EP	7.0		
PAUSE/S	0.0	REMARKS	
EP-CRIT	5.0		
ADD V/ML	0.000		
EP-M LIM1	0.000		
PH LIM2	14.000		
0105			

Figure 7b. Simultaneous Determination of HAN and IPAN by Titration After Formation of Acetoxime by Acetone Addition; First Derivative.

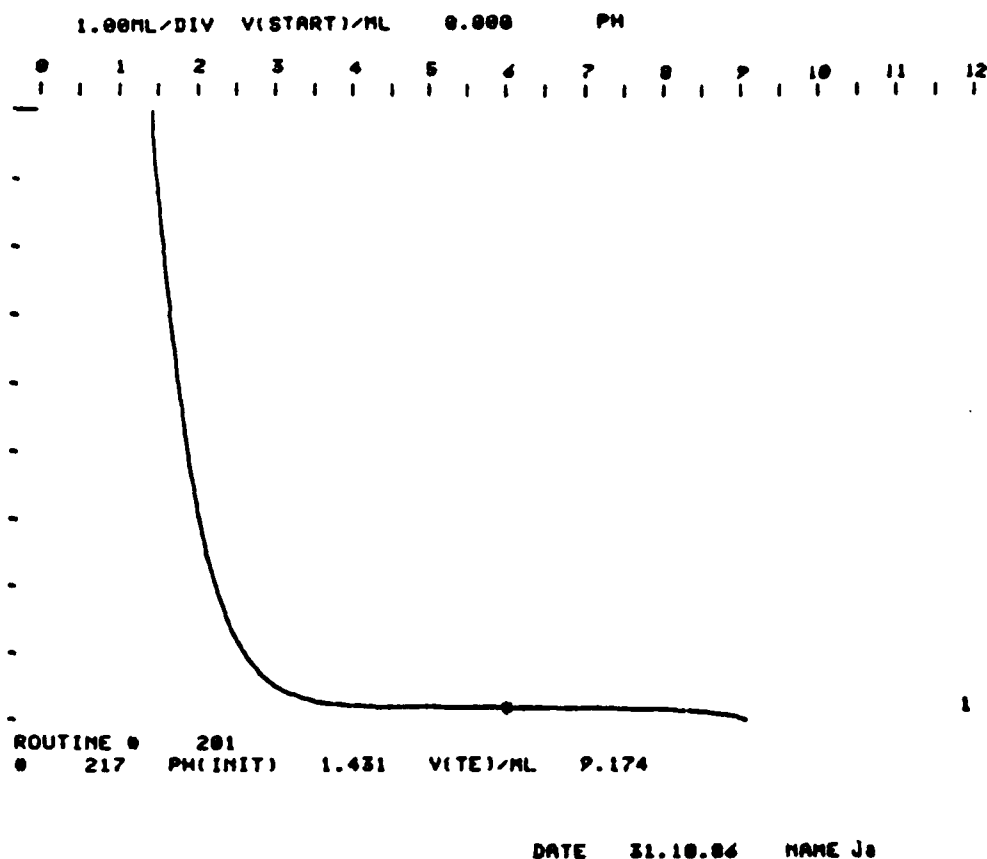
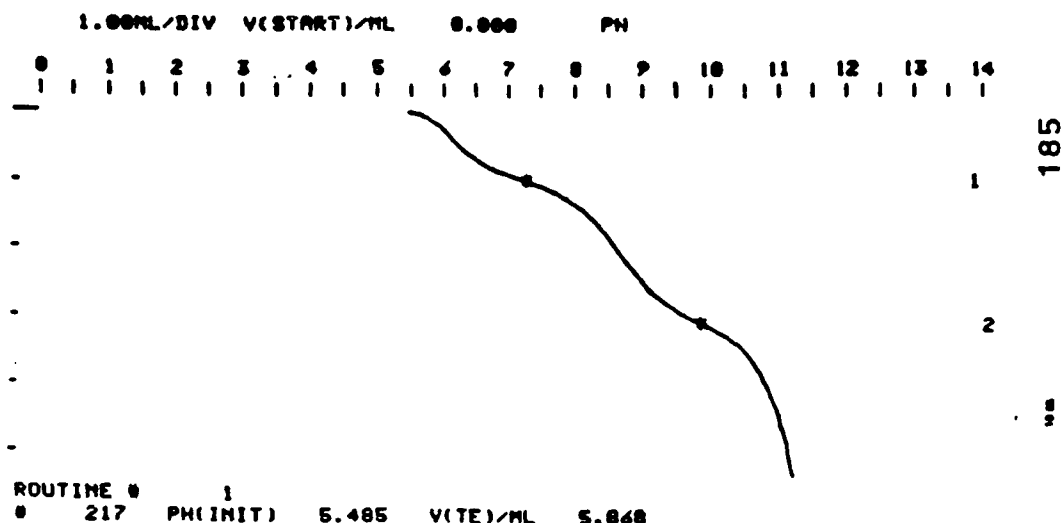


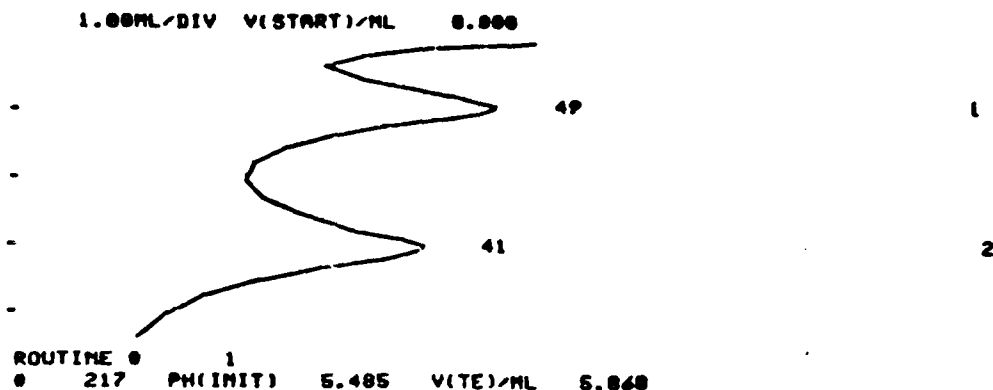
Figure 8a. Simultaneous Determination of HAN, IPAN, and AN by Titration: Determination of HAN After Formation of Acetoxime by the Addition of Acetone.

differences are dependent on the quantity of ammonium nitrate in the sample. Corrections are complicated and cannot be used with confidence. AN can be determined using the Ströhlein apparatus, originally designed for the determination of nitrogen in steels. The method is based on the steam distillation of ammonia from alkaline solution. The technique is applicable because triethanolamine is not volatile in steam. Hydroxylamine in the sample is first oxidized quantitatively to nitrous oxide, N_2O , with Fehling's solution, a Cu^{2+} -tartrate complex in alkaline solution. Ammonia is not a product of this oxidation. The Ströhlein distillation apparatus is shown in Figure 11 and described diagrammatically in Figure 12. Steam is generated in an electric boiler (3), conducted through a distillation flask (7) after spray separation, and is then condensed in dilute boric acid in a Volhard receiver (8). The ammonia collected is then titrated with hydrochloric acid. The apparatus permits repeatable determination of AN in quantities as small as 0.1 wt.-%. Since both ammonium nitrate and free nitric acid are present only in small amounts, the analytical methods were carefully evaluated by adding known amounts of ammonium nitrate or nitric acid to samples of propellant.



DATE 31.10.86 NAME Ja

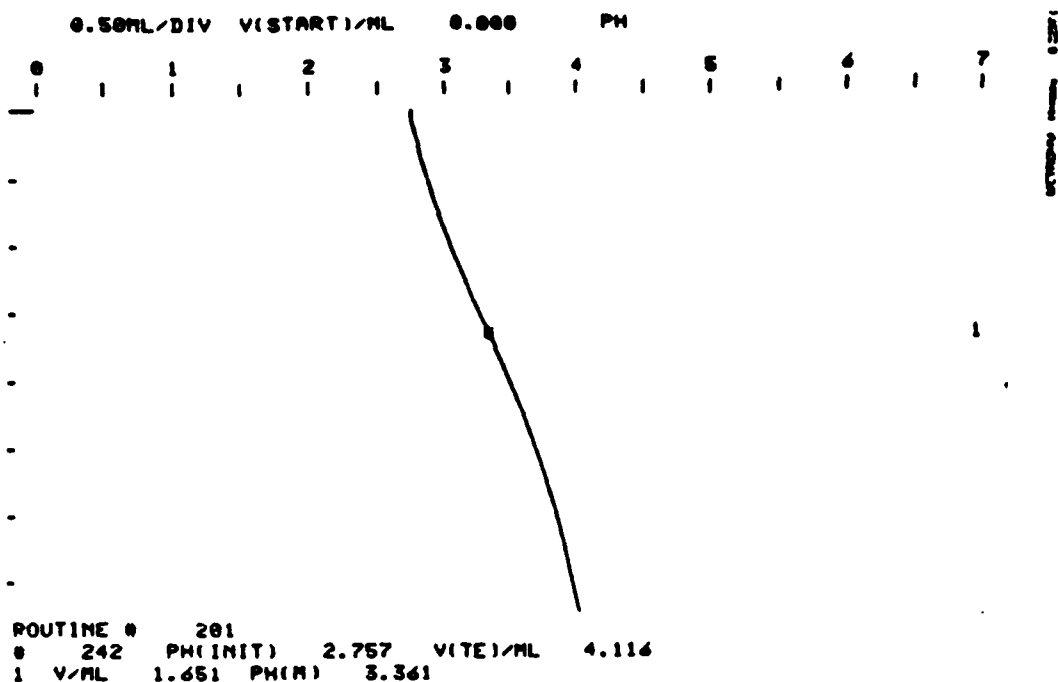
BUR.2 V/ML 10.0 ROUTINE # 201
TEMP/C 25.0 REAGENT 0,5 n NaOH w&Br. Titrisol
KINET D 0.0 TITER 1,000
MPD VAR 0.0 ELECTRODES 2 kumbinierte Glaselktrode Metrohm
START V/ML 0.000
STOP PH 100.000 SAMPLE 722,6 mg NOS 365 + 10 ml Aceton (HAN-Best.)
STOP V/ML 10.000 + 5 ml Formaldehyd 37 %
STOP # EP 9.0 + 406,9 mg NH₄NO₃ Lsg. (=38,61 mg 100 %)
PAUSE/S 0.0
EP-CRIT 5.0 REMARKS
ADD V/ML 0.000
EP-W LIM1 0.000
PH LIM2 14.000
0105



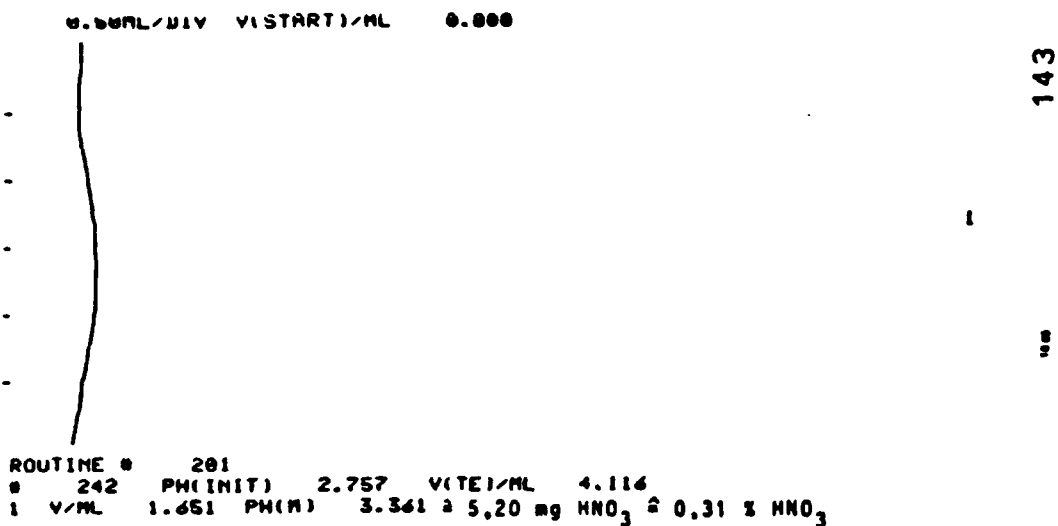
DATE 31.10.86 NAME Ja

- 1) Determination of AN After the Addition of a known Quantity of Ammonium Nitrate and the Addition of Formaldehyde (Formation of Hexamethylene Tetramine).
- 2) Determination of IPAN.

Figure 8b. Simultaneous Determination of HAN, IPAN, and AN by Titration: Titration Curve (top) and 1st Derivative (bottom).



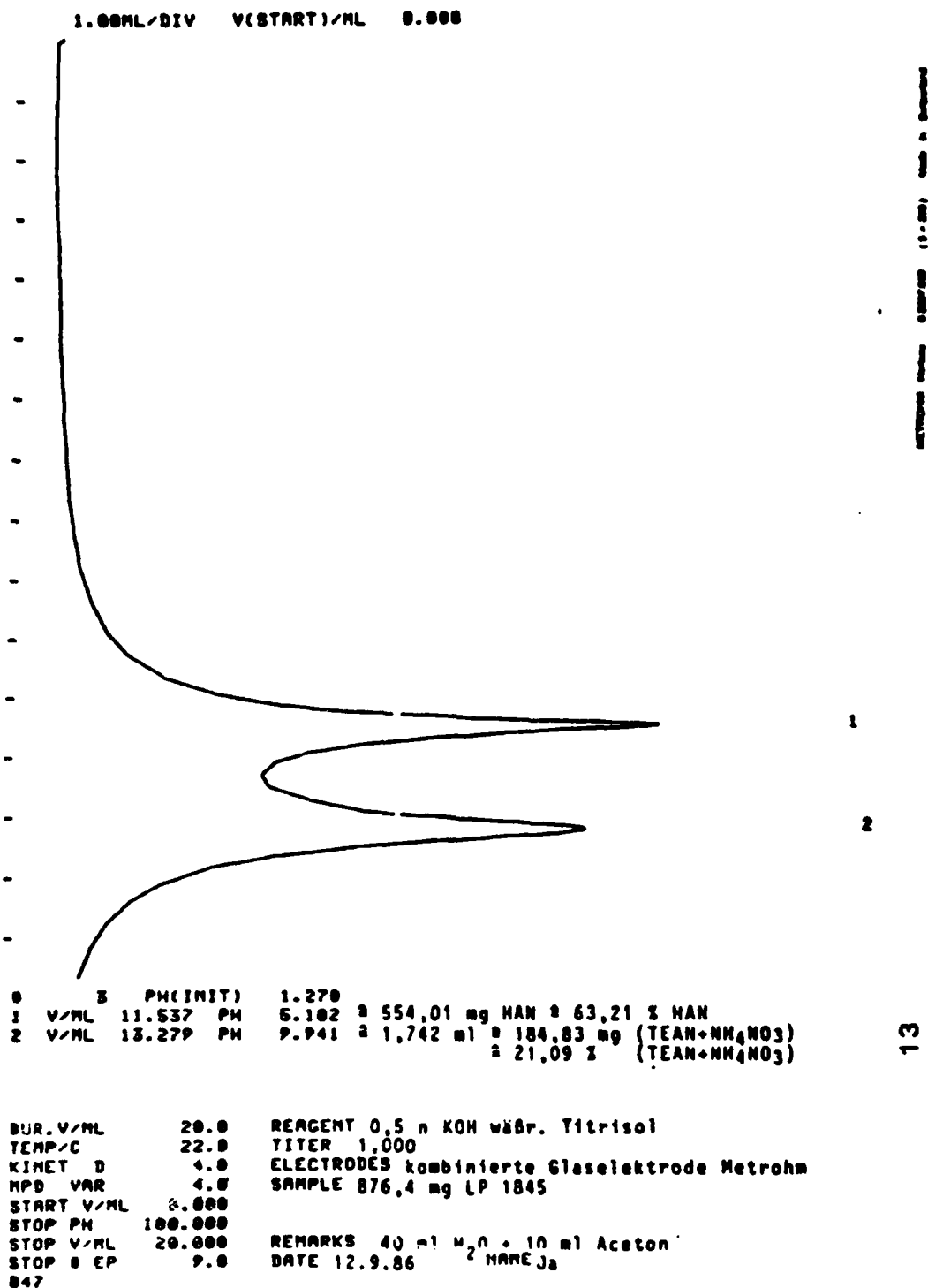
DATE 10.11.84 NAME



DATE 10.11.84 NAME Ja

BUR.2 V/ML	10.0	ROUTINE #	201
TEMP °C	21.0	REAGENT	0,05 n NaOH wäBr.
KINET D	0.0	TITER	1,000
MPD VAR	0.0	ELECTRODES	2 kombinierte Glaselektrode Metrohm, geeicht.
START V/ML	0.000	SAMPLE	1672,3 mg IP 1845, Thiokol
STOP PH	100.000	REMARKS	Säurebestimmung
STOP V/ML	10.000		
STOP # EP	9.0		
PAUSE/S	0.0		
EP-CRIT	5.0		
ADD V/ML	0.000		
EP-W LIM1	0.000		
PH LIM2	14.000		
0105			

Figure 9. Determination of Free Nitric Acids in LGP1845:
Titration Curve (top) and First Derivative (bottom).



1) Determination of HAN After Acetoxime Formation
by the Addition of Acetone.

2) Determination of TEAN.

Figure 10b. Analysis of LGP1845: Simultaneous Determination
of HAN and TEAN by Titration: First Derivative.

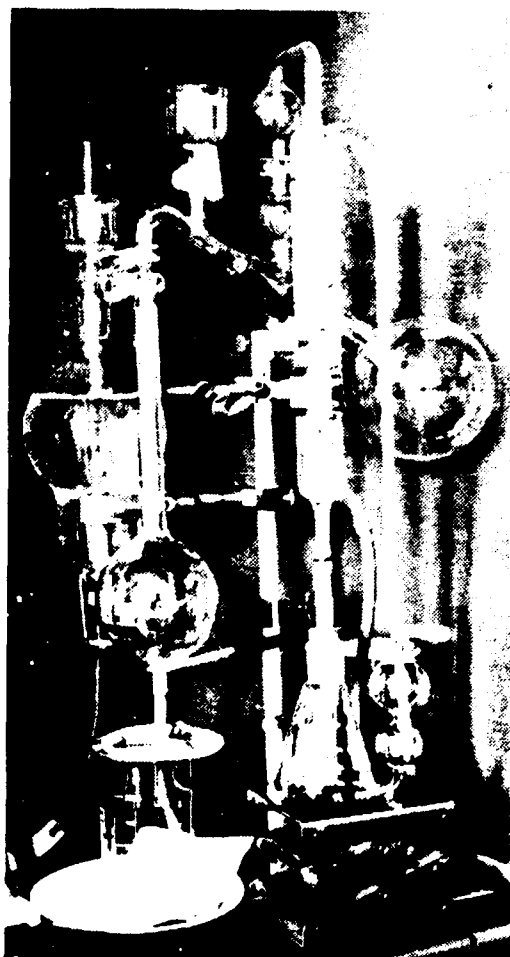
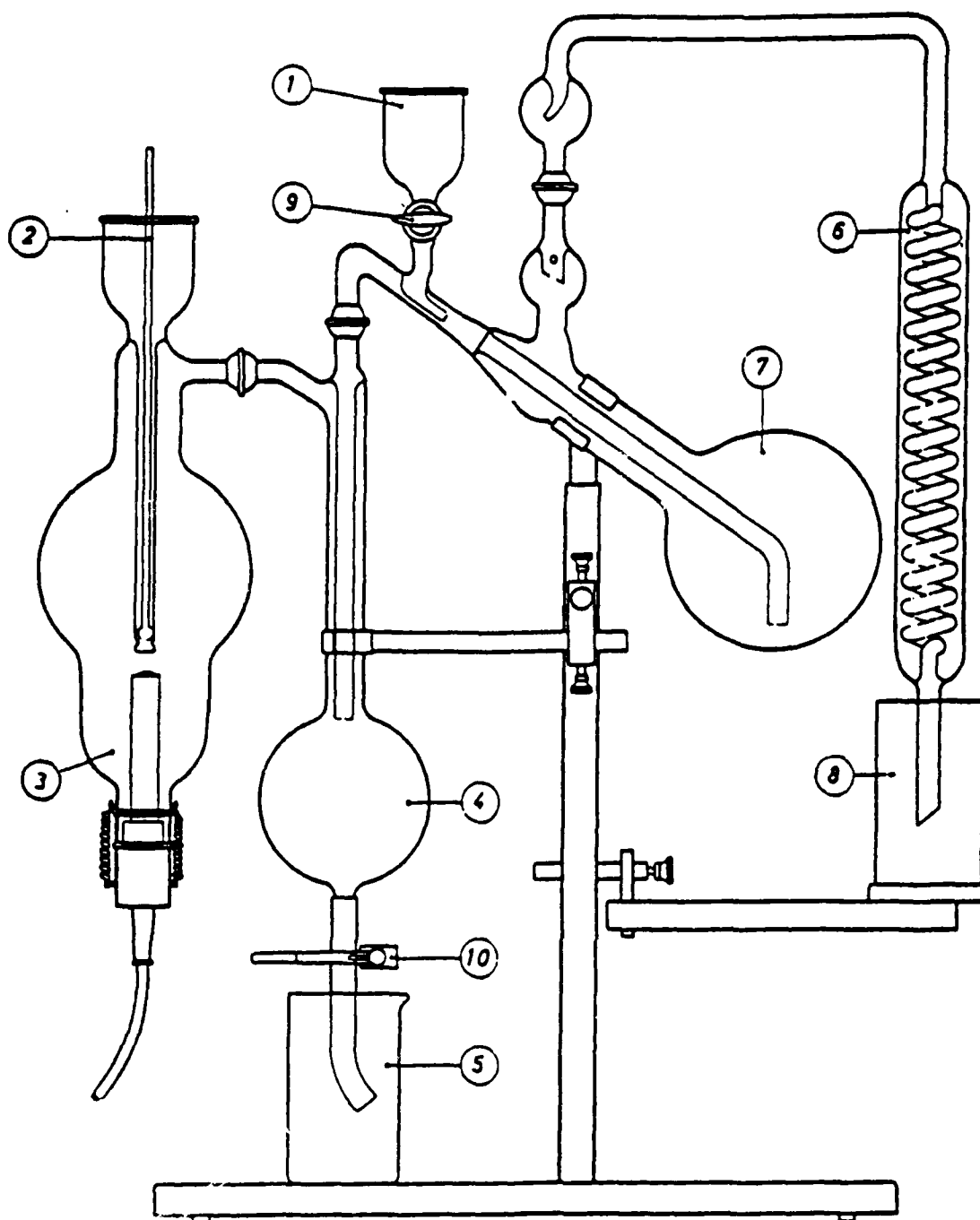


Figure 11. Ströhlein Steam Distillation Apparatus.

The water content of the propellants can be determined by Karl Fischer titration. This method requires a special titration apparatus because the Titroprozessor 636 is not suited for this type of titration. The presence of amines and particularly the reducing ability of hydroxylamine may cause interference. Such interferences can be avoided by following the recommendations of Riedel de Haen, the manufacturer of the Karl Fischer reagent used (Firmenschrift der Riedel 1982). The composition of various LGP1845 and LGP1846 mixtures is given in Table 8. Significantly more AN is seen in the LGP1846 prepared from HAN supplied by BASF than is present in either LGP1846, lot 49-1, or in the LGP1845 prepared from Thiokol-supplied HAN. Metal content was determined by atomic absorption spectroscopy.

5.6 Precision of the Analytic Determinations. If, in the chemical analysis of a quantity X, (the HAN content in wt.-%, for example), n individual determinations are made, the most probable value is the arithmetical mean:

$$\bar{X} = \Sigma X/n. \quad (5)$$



- | | |
|-----------------------|------------------------|
| (1) Sample Inlet | (6) Spiral Condenser |
| (2) Boiler Inlet Tube | (7) Distilling Flask |
| (3) Electric Boiler | (8) Product Collection |
| (4) Spray Trap | (9) Stopcork |
| (5) Waste | (10) Pinchclamp |

Figure 12. Diagrammatic Representation of the Ströhlein Steam Distillation Apparatus.

Table 8. Analysis of Several Propellants.

LP-Type	LGP1846	LGP1845	LGP1846
HAN-producer or LOT-No.	BASF	THIOKOL	LOT 49-1
HAN [wt-%]	60.04	63.01	61.43
TEAN [wt-%]	18.37	20.14	18.54
H ₂ O [wt-%]	19.49	16.07	19.50
NH ₄ NO ₃ [wt-%]	2.10	0.47	0.53
HNO ₃ [wt-%]	0.00	0.31	0.00
HNO ₃ [moles/l]	0.00	0.05	0.00
pH (diluted 1:1)	2.741	0.974	1.705
Density 25 °C [g/cm ³]	1.462	1.466	1.445
<u>Metals</u>	<u>Detection</u>		
	<u>Limit</u>		
Cu	0.1	0.02	0.02
Zn	0.2	-	-
V	1.7	<1.9	<2.0
Cr	0.2	0.33	0.13
Mo	0.6	<2.0	<2.0
W	11.0	<11	<11
Mn	0.05	0.00	0.03
Fe	0.1	0.90	0.10
Ni	0.1	0.37	0.26
Sn	1.0	-	-
Na	0.1	-	-

As a measure of scatter of the individual values, the standard deviation s is most frequently used (Jander and Jahr 1986; Kaiser and Gottschalk 1972):

$$s = \sqrt{\frac{(X - \bar{X})^2}{n - 1}} = \sqrt{\frac{\sum X^2 - (\sum X)^2/n}{n - 1}} \quad (6)$$

\bar{X} and s are dimensionally the same, and mol/kg or percentage by weight (wt.-%) are common units in chemical analysis. The measurements are more precise when \bar{X} is large and s is small. The coefficient of variance V , where:

$$V = s \cdot 100 / \bar{X} \quad (7)$$

is normally expressed in percent and is a useful parameter for expression of relative error. Typical values obtained for HAN, TEAN, AN, and HNO₃ are listed in Table 9. It was not always feasible, unfortunately, to carry out a large enough number of determinations to substantially reduce V. It can nevertheless be seen that HAN, the largest propellant component, can be determined with the greatest precision. The coefficient of variance is between 0.12 and 0.18%. The determination of TEAN is less precise, V having a value of 1.1-1.9%. For ammonium nitrate, the value of V is highest, 13.7%. This is principally due to the fact that determination of AN is the most difficult individual measurement in the propellant analysis. However, the comparatively high relative error is tolerable because of the low AN concentrations involved. Free nitric acid is also present in small quantities, but the determination is simpler, and, hence, the variance coefficient is 2.6%.

Table 9. Typical Values of \bar{X} , s, V, and n for Propellant Analyses.

Propellant	Component	\bar{X} in wt.-%	s in wt.-%	V in rel. %	n
LGP1845	HAN	62.90	0.12	0.1	12
	TEAN	19.77	0.38	1.91	12
	AN	0.47	0.06	13.7	2(!)
	HNO ₃	0.31	0.0082	2.63	4
LGP1846	HAN	61.37	0.074	0.121	11
	TEAN	18.60	0.2	1.07	3
	AN	0.53	--	--	3
	HNO ₃	0	--	--	-

6. TEST RESULTS

6.1 The Storage of LGP1846 in Glass Ampoules.

6.1.1 The Influence of Metals and Non-Metals on the Thermal Stability of LGP1846.

Accelerated storage tests were carried out in sealed glass ampoules in order to determine the effects of metals on the storage life of LGP1846. The time to ampoule bursting at 90° C and relative lifetimes are listed in Table 10. Metals were added in the form of filings or powder. The time to the bursting of the ampoule is an indication of the compatibility of the propellant with the metal. The ratio of this time and the time to bursting of the non-contaminated propellant is the relative lifetime, the value of the original LGP1846 being 100%. Observed changes in either the propellant or the additive are recorded in the last column of Table 10. Gold, silver, and mercury had no

Table 10. The Effect of Metals and Alloys on the Thermal Stability of LGP1846.

Metal	Decomposition time in days	Relative decomposition time in %	Remarks
- (Original LP)	68.6	100.0	colourless
Lead	70.3	102.5	"
Silver	70.1	102.2	"
Tantalum	69.9	101.8	"
Gold	69.5	101.5	"
Zinc	69.2	100.9	dissolved
Mercury	68.2	99.0	colourless
Manganese	67.8	98.8	dissolved
Aluminium	63.4	92.4	colourless
Iridium	62.0	90.4	"
Silicon	57.0	83.1	"
Nickel	56.8	82.8	green
Cobalt	55.6	81.0	pink
Platinum	56.7	82.7	colourless
Molybdenum	47.8	69.7	dissolved
Tin	45.0	65.6	dissolved
Titanium	42.0	61.2	colourless
Tungsten	34.4	49.7	"
Chromium	23.4	34.1	"
Antimony	4.0	5.8	"
Copper	1.6	2.3	green
Rhenium	1.5	2.2	colourless
Iron	1.0	1.5	yellowish-green
<u>Alloys</u>			
V 4A (1.4571)	50.4	73.5	colourless
17/4 PH (pressure transducer) (1.4542)	15.7	22.9	"
V 2A (1.4541)	1.8	2.6	"
30 Cr Ni Mo 8 V (1.6582)	0.8	1.1	"
35 Ni Cr Mo V 125 (1.2760)	0.5	0.7	colourless

effect on the storage life of LGP1846. Some of the metals dissolved in the propellant, undoubtedly as complex ions. In spite of the chemical reactions involved, the time to bursting of the ampoules was equal to that of uncontaminated propellant in the case of zinc and 10% longer in the case of manganese. Both lead and aluminum partially dissolved in LGP1846 but did not significantly change time to bursting. This apparently anomalous behavior is readily explained. The measure of storage life in these tests is related exclusively to gas production so that reactions that do not result in the production of gaseous decomposition products appear to have no effect on storage life. The majority of the metals added shortened storage life, some--like copper, rhenium, and iron--by more than 90%.

The composition of the steels tested is given in Table 11. All significantly shortened the storage life of the liquid propellant. Thus, the storage life of LGP1846 is reduced to 74% when in contact with V 4A, and to 3% with V 2A. 17-4 PH, the alloy used in the pressure transducers, shortens the storage life of the propellant to 23% of uncontaminated LGP1846. Two gun steels, German Standards No. 1.6580 and No. 1.2760, cause the ampoules to burst within one day.

Table 11. The Composition of Stainless Steels.

Material Material No.	17/4 PH 1.4542	V 2A 1.4541	V 4A 1.4571	30 Cr Ni Mo 8V 1.6580	35 Ni Cr Mo V 125 1.2760
C	< 0.07	≤ 0.06	0.60	0.26-0.33	0.35
Si	< 1	≤ 1	≤ 1	0.25	0.2
Mn	< 1.00	≤ 2	≤ 2	0.45	0.5
P	< 0.04			0.035	
S	< 0.03				
Cr	15.5-17.5	17-19	16.5-18.5	2.0	1.4
Mo	-		2-2.5	0.4	0.3
Ni	3.00-5.00	9-11.5	10.5-13.5	2.0	4.0
Cu	3.00-5.00				
Nb + Ta	0.15-0.45				
Ti		0.3	0.3		

Various plastomers and elastomers that were considered for use in the pressure recording apparatus are described in Table 12. Test results are shown in Table 13. It can be seen from this table that ethylene-propylene-diene copolymers (EPDM), ethylene-propylene copolymers (EP), and Viton (FPM) reduce the storage life of the propellant to approximately the same extent as do the stainless steels.

Table 12. Polymers Considered as Sealing Materials.

Chemical Name	Abbreviation	Colour	Supplier
Ethylene-Propylene-Diene Copolymers	EDPM	black	Freudenberg, D-6940 Weinheim, FRG
Vinylidene-fluoride-Hexafluoropropylene Copolymers (Viton)	FPM	black-brown	Ulman, D-7032 Sindelfingen 6, Otto-Hahnstr. 17, FRG
Acrylonitrile-Butadiene Copolymers	NBR	black	Freudenberg (as above)
Silicone Resin	VMQ	red	Ulman (as above)
Ethylene-Propylene Copolymers	EP	black	Ulman (as above)
Polytetrafluoroethylene	PTFE (PT 950)	white	Gehreckens, D-2080 Pinneberg, FRG
Polytetrafluoroethylene	PTFE (TFM)	white	Beichler & Grünewald, 7121 Lochgau, FRG
Tetrafluoroethylene-Perfluoroalkylvinyl Ether Copolymers	PFA, TFA	opalescent-white	Beichler & Grünewald
Polytrifluorochloroethylene	PCTFE	transparent-turbid	Beichler & Grünewald
Perfluorelastomer	Kalrez 4079	black	Du Pont, D-4000 Düsseldorf, FRG

Table 13. The Influence of Sealing Materials on the Thermal Stability of LGP1846 at 90° C.

Sealing Material	Decomposition time in days		Relative decomposition time in %	
	in contact with LP	in gas space	in contact with LP	in gas space
- (original LP)	86.5	86.5	100	100
EPDM	6.2	20.7	7.2	23.9
FPM (Viton)	18.7	19.0	21.6	21.9
NBR	20.6	19.1	23.8	22.1
VMQ	44.8	61.9	51.7	71.6
EP	6.5	22.1	7.5	25.5
PTFE (PT 950)	86.2	not determined	99.6	not determined
PTFE (TFM)	88.6	"	102.4	"
PFA, TFA	90.6	"	104.7	"
PCTFE	94.0	"	108.6	"
Kalrez 4079	36.8	"	42.5	"

6.1.2 Effect of pH on the Stability of LGP1846. As pH is raised, HAN and TEAN dissociate, releasing the respective amines. The propellant acts as a buffer in the vicinity of pH 4. Since hydroxylamine is less stable than its salts, we initially assumed that an excess of nitric acid should increase the stability of the propellant. Preliminary data, obtained with a HAN-IPAN propellant mixture, indicated that an optimum pH for storage stability exists.

The acidity of LGP1846 samples was adjusted with nitric acid or solid magnesium oxide. MgO was selected because Mg^{2+} does not appear to affect propellant stability and because MgO does not alter oxidizer-to-fuel ratio as the addition of hydroxylamine would. pH was measured on propellant samples that had been diluted 1:1 with water. Our tests covered the pH range 0.7 to 4.3. Storage stability results are shown in Table 14. Maximum stability is seen in the region between pH 2.0 and 2.6. In strongly acidic samples ($pH < 1.9$), time to ampoule bursting decreases rapidly, changing from 86 to 60 days. The decrease in storage life changes gradually at pH values greater than the optimum, and at a pH of 4.3, the storage life has only decreased to 80 days.

6.1.3 The Influence of Metal Ions on the Thermal Stability of LGP1846. We examined the effect of metal ions on thermal stability as a function of concentration, covering the range 0.5 to 100 ppm. Where possible, only the nitrate salts of the metals were used so that the effect of anions such as chloride or sulfate was eliminated. However, a number of the metals were only available in the form of their oxides and had to be used as such. In cases where metal salts were available in more than one oxidation state, the most stable salt was used. Test conditions were the same as previously described. Table 15 summarizes the results obtained. Relative stability compared with metal-free propellant is listed as a function of metal concentration in the range of 2 to 100 ppm. The ions are listed in order of decreasing storage life at the 100 ppm concentration. The ions listed in the first group have little or no effect on time to bursting of the ampoules up to concentrations of 100 ppm. Those ions that cause a decrease in storage stability show a clear concentration dependence. Although a number of ions require concentrations greater than 10 ppm to produce a measurable effect in these tests, others--notably iron, copper, and vanadium--produce a decrease in storage life at concentrations as low as 2 ppm. These ions were evaluated at 0.5 and 1 ppm in addition to the higher concentrations and results are listed in Table 16. Palladium is included in Table 16 for comparison. In contrast to the palladium data, iron, copper, and vanadium ions clearly decrease storage life at concentrations of 0.5 ppm. Clearly, these ions should be excluded from the HAN-based propellants.

Table 14. Storage Duration of LGP1846 as a Function of pH Value.

pH Value at 1:1 dilution	Decomposition time in days
0.71	60.5
0.88	67.6
1.21	78.0
1.50	83.5
1.86	84.2
2.09	86.8
2.33	85.9
2.68	86.2
3.00	84.5
3.25	83.4
3.46	82.6
3.65	81.8
3.85	81.2
4.29	80.1

6.1.4 Attempts to Improve the Stability of Contaminated LGP1846. The addition of stabilizers to conventional solid gun propellants slows decomposition generally by reacting with the oxides of nitrogen. Urea and its carbamide derivatives and other very weak bases have been found to be effective stabilizer additives. The oxides of nitrogen react rapidly with the HAN-based propellants, more rapidly, in fact, than with the stabilizers used in solid propellants. The addition of such "stabilizers" will, therefore, not result in any notable increase in liquid propellant storage life. Although no trials have been carried out to test urea derivatives and similar substances as HAN stabilizers (BASF 1987; Carlos 1970), an effective stabilizer will most probably function in a different way because a prominent mode of HAN decomposition is based on the catalytic effects of a number of metal ions.

The reaction mechanism presented for propellant decomposition in Section 3 indicates that pure hydroxylammonium nitrate thermally decomposes, producing inert nitrous oxide, N_2O . Nitrous acid, HNO_2 , which is formed in a secondary reaction, reacts with the large excess of HAN, producing additional N_2O . A stabilizer that would neutralize nitrous acid and/or N_2O_3 is therefore not necessary. Metal ions, such as Fe, Cu, and V, accelerate the formation of the intermediate compound dihydroxylamine, and all attempts at stabilization must therefore be directed toward reduction of the metal ion concentration. It has been our aim to suppress propellant decomposition by complexing the metal ions. Unfortunately, most metal ion complexes are not especially stable at

Table 15. Comparison of the Relative Decomposition Times of Metal Ion Contaminated LGP1846. Metal-Free Propellant = 100%.

Metal Ion Concentration (ppm)	Relative Decomposition Time in %			
	2	5	10	100
W ⁶⁺	115	120	103	104
Zr ⁴⁺	104	98	100	102
Cr ³⁺	-	-	(92)	100
Mn ²⁺	106	102	101	97
Mg ²⁺	-	98	95	96
Pb ²⁺	94	88	87	96
Sn ²⁺	103	98	100	92
Ag ²⁺	101	99	93	92
Ce ⁺	103	98	(80)	91
Zn ²⁺	99	100	(84)	90
Ni ²⁺	105	97	99	89
Al ³⁺	101	88	(80)	87
Cd ²⁺	96	94	(80)	86
B ³⁺	102	97	96	85
Co ²	100	99	97	80
Hg ²⁺	98	100	102	79
Mo ⁶⁺	-	-	98	69
Ti ⁴⁺	109	95	98	(66)
Bi ³⁺	93	100	93	54
Pd ²⁺	101	94	78	52
Cu ²⁺	73	59	48	17
V ⁴⁺	71	59	40	13
Fe ³⁺	55	36	24	4
Fe ²⁺	57	31	20	4

Table 16. Comparison of the Relative Decomposition Times of LGP1845 Containing Various Metal Ions.

Metal Ion Concentration (ppm)	0,5	Relative Decomposition Time in %				100
		1	2	5	10	
PD ²⁺	98	100	101	94	78	52
Cu ²⁺	84	87	73	59	48	17
V ⁴⁺	89	88	71	59	40	13
Fe ²⁺	77	71	57	31	20	4

the pH of the HAN-based propellants. The pH-dependent dissociation equilibrium of these complexes results in sufficient concentrations of the metal ions to catalyze the decomposition of the hydroxylammonium nitrate.

It is the initial aim of all HAN-processing procedures to prevent decomposition by avoiding metal ions. Such a requirement can only be realized with difficulty under practical or near-practical conditions, and, therefore, the effects of metal ions must be suppressed via stabilizers. A number of methods have been proposed to solve these problems, such as the transfer of metal ions into very stable complexes (Moews 1959). However, in practice, this is restricted because most complexes are sufficiently stable. Alternately, other complexes are only stable in organic systems and are, under certain circumstances, only suitable for the extraction of metal ions. A further possibility lies in removing the metal ions from the propellant using ion-selective, matrix-bonded substances. Removal of the disturbing metal ions might also be achieved via precipitation with appropriate reagents.

If it were possible to demonstrate a reduction in decomposition by addition of a complex-forming reagent, it would consequently be worthwhile to pursue this approach to increased propellant stability. Attempts were made to reduce the decomposition of copper- and/or iron-contaminated LGP1846 using the variety of complex-forming reagents listed in Table 17. All tests were carried out in ampoules at 90° C using 200 ppm of the complexing agents and 100 ppm of the metal ions. Results indicate no increase in thermal stability with any of the substances tested.

Among the potential stabilizers investigated were a number of commercially available products marketed as water softeners. These substances form heavy metal complexes which are stable in acidic media. No detailed information is available at the present time concerning the equilibrium constants for complex formation which will probably have different values for each metal ion. The equilibrium constants would have to be determined for substances that demonstrate their efficacy in our tests. Table 18 lists several of this type of complexing agent, their chemical composition, and their suppliers. Their effect on propellants contaminated with iron or copper ions is shown in Table 19. A small stabilizing effect is seen with quinoline-2-carboxylic acid, α -dimethylglyoxime, and Turpinal D2 and copper-contaminated propellant. Dequest 2041, Dequest 2056, and Turpinal D2 showed significant improvements in the stability of iron-containing propellant samples. At higher concentrations, a number of stabilizers caused turbidity in the propellant liquid, and the potential effects of sludge formation should be considered. In some cases, the stabilizers produced characteristically colored complexes with the metal ions, leading to the possibility of a simple test for impurities.

Table 17. The Influence of Potential Stabilizers on the Thermal Decomposition of LGP1846 Containing Copper or Iron Ions.

Stabilizer Content (200 ppm)	LGP1846 (Lot 49-1)	
	Decomposition Time In Days	
	Cu ²⁺ (100 ppm)	Fe ²⁺ (100 ppm)
- (without stabilizer)	15.9	3.5
Potassium fluoride	12.8	2.9
Tartaric acid	12.7	3.0
Citric acid	13.1	3.1
Phosphoric acid	12.2	3.5
8-Hydroxyquinoline	15.0	2.4
Nitrosophenylhydroxylamine (NH ₄)	7.4	3.4
Dimethylglyoxime	12.6	2.7
Resorcin	12.1	2.1
Pyrocatechol	11.9	2.9
Morin	12.1	3.2
Alizarin	12.0	2.1
Alizarin monosulfonic acid (Na)	13.0	2.3
Ellagic acid	12.4	2.1
Dithizone	7.7	2.0
2,2'-dihydroxydiphenyl	12.8	3.2
Aurintricarboxylic acid (NH ₄)	16.0	2.9
2-Hydroxy-5-methyl-1-azobenzene	11.7	2.9
5-Amino-salicylic acid	11.9	2.8
Ethylene diamine tetraacetic acid	6.4	3.2
3-Hydroxydiphenylamine	12.4	2.8
2,5-Dihydroxybenzaldehyde	13.1	3.2
Gallic acid	8.1	4.5
Dicyclohexyl-18-crown-6*	10.1	3.1
12-crown-4*	7.4	3.3
15-crown-5*	7.9	2.0
Dibenzo-18-crown-6*	7.2	2.1

* Supplier: E. Merck AG, FR Germany

Table 18. Selection of Complexing Agents.

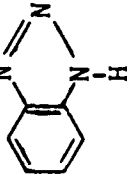
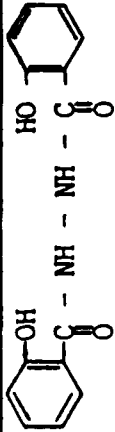
Trade Name	Structural Formula	Chemical Name	Supplier
Turpinal SL	$\begin{array}{c} \text{HO} \quad \text{CH}_3 \quad \text{OH} \\ \quad \quad \\ \text{HO} - \text{P} - \text{C} - \text{P} - \text{OH} \\ \quad \quad \\ \text{O} \quad \text{OH} \quad \text{O} \end{array}$	1-Hydroxy-ethylidene-1,1-disphosphonic acid	Henkel KG Postfach 11 00 D-2000 Düsseldorf
Turpinal D 2	$\text{N} \left(- \text{CH}_2 - \text{P} \begin{array}{c} \text{O} \\ \\ \text{OH} \end{array} - \text{OH} \right)_3$	Amino-tris-(methylene phosphonic acid)	Henkel KG
Remomet BTA-M		Benzotriazole	Ciba-Geigy CH-4002 Basel
GI 09-215/3		N,N'-Disalicyloylhydrazine	Ciba-Geigy
Dequest 2000	Identical with Turpinal D 2	see above	Brenntag AG Postfach 10 03 52 4330 Mülheim-Ruhr 1
Dequest 2010	Identical with Turpinal SL	see above	Brenntag AG
Dequest 2041	$\left(\text{HO} - \text{P} \begin{array}{c} \text{OH} \\ \\ \text{O} \end{array} - \text{CH}_2 \right)_2 \text{N}(\text{CH}_2)_2 \text{N} \left(- \text{CH}_2 - \text{P} \begin{array}{c} \text{OH} \\ \\ \text{O} \end{array} - \text{OH} \right)_2$	Ethylenediamine-tetra-(methylene phosphonic acid)	Monsanto Europe N.V. Scheldelaan B-2040 Antwerpen
Dequest 2060 S	$\text{HO} - \text{P} \begin{array}{c} \text{OH} \\ \\ \text{O} \end{array} - \text{CH}_2 - \text{N} \left[- \text{CH}_2 \text{CH}_2 \text{N} \left(- \text{CH}_2 - \text{P} \begin{array}{c} \text{OH} \\ \\ \text{O} \end{array} - \text{OH} \right)_2 \right]_2$	Diethylenetriamine-penta-(methylene phosphonic acid)	Monsanto Europe N.V.
Dequest 2056	$\left(\text{HO} - \text{P} \begin{array}{c} \text{OH} \\ \\ \text{O} \end{array} - \text{CH}_2 \right)_2 \text{N}(\text{CH}_2)_6 \text{N} \left(- \text{CH}_2 - \text{P} \begin{array}{c} \text{OH} \\ \\ \text{O} \end{array} - \text{OH} \right)_2$	Hexamethylenediamine-tetra-(methylene phosphonic acid)	Monsanto Europe N.V.

Table 19. The Influence of Stabilizers on the Decomposition of
LGP1846 Contaminated With 100 ppm Copper Iron Ions.

Stabilizer	Decomposition Time In Days	
	Cu ²⁺ (100 ppm)	Fe ²⁺ (100 ppm)
- (without stabilizer)	15.9	3.5
Turpinal SL	17.2	4.2
Turpinal D2	19.3	6.0
Dequest 2041	15.4	13.5
Dequest 2060 S	4.0	5.0
Dequest 2060 S (free from HCL)	17.1	5.0
Dequest 2056	1.5	7.5
Dequest 2056 (free from HCL)	16.3	-
Benzotriazole	14.5	3.0
N,N'-Disalicyloyl-hydrazine	15.1	3.0
1-Nitroso-2-naphthol	15.2	3.0
1,2-Cyclohexanedione	17.9	3.0
α -Dimethylglyoxime	19.8	3.0
Tris [2-(2-methoxy-ethoxy)-ethyl]amine	16.8	4.5
Quinaldine acid	20.3	4.5
Thioglycolic acid	18.9	4.5
Dithiooxamide	17.8	4.0
Titriplex II (EDTA)	16.3	4.5
Titriplex IV (CDTA)	16.9	5.2
Urea	18.0	3.5
Zincon	11.6	2.9
Tributylphosphate	2.0	5.5
2,4,6-Tri-(2-pyridyl-s-triazine)	19.7	4.5
Nitroso-R-salt	15.3	4.0

A number of chelating agents are capable of forming multidentate bonds and molar ratios of metal ions and complexing agents of 1:1 and 1:10 were selected for our tests. Results of tests with propellant containing 10 ppm iron are shown in Table 20. It can be seen that the organic polyaminophosphonic acids show a significant stabilizing effect. The increases in storage life were greater at a molar ratio of 1:10. The addition of Turpinal D2 caused an increase in storage life of the propellant from 15.4 to 42.5 days, a factor of 2.4. These factors were 2.7 for Dequest 2041 and 2.2 for (HCL free) Dequest 2060 S. Dequest 2060 S, as usually supplied, contains 16% hydrochloric acid, and this preparation actually shortens storage life. Purification of the as-supplied Dequest 2060 S results in an acid-free product with the stabilizing properties shown. The remaining substances listed in Table 20 showed little or no stabilizing effect. According to our measurements, α - α' -dipyridyl, a well-known iron complexing reagent, exhibited virtually no stabilizing effect.

Table 20. The Effect of Iron-Stabilizer Ratio on the Decomposition of LGP1846 Contaminated With 10 ppm Iron Ions.

Stabilizer	Iron : Stabilizer 1 : 1 in moles	Iron : Stabilizer 1 : 10 in moles
- (without stabilizer)	17.4	17.4
Turpinal SL	19.8	25.0
Turpinal D2	34.2	42.5
Dequest 2041	29.2	47.4
Dequest 2060 S	18.3	11.8
Dequest 2060 S (free from HCL)	-	39.0
Dequest 2056	-	19.5
Dequest 2056 (free from HCL)	-	-
Benzotriazole	-	18.4
N,N'-Disalicyloyl-hydrazine	-	19.2
1-Nitroso-2-naphthol	-	26.7
1,2-Cyclohexanedione	-	19.7
α -Dimethylglyoxime	-	20.6
Tris [2-(2-methoxy-ethoxy) - ethyl]amine	-	20.8
Quinaldine acid	-	18.2
Thioglycolic acid	-	19.2
Dithiooxamide	-	18.9
Titriplex II (EDTA)	-	21.0
Titriplex IV (CDTA)	-	25.1
Urea	-	19.1
Zincon	-	17.3
Tributylphosphate	-	22.5
2,4,6-Tri-(2-pyridyl-s-triazine)	-	19.3
Nitroso-R-salt	-	19.1
α , α' - Dipyridyl	-	19.2

6.1.5 The Collective Influence of Copper and Iron Ions (Synergistic Effect). Attempts were made to determine whether the presence of both Cu and Fe ions produced a synergistic effect on decomposition rate. Results are shown in Table 21. The rate of gas production for iron-containing propellant is much higher than for propellant containing copper. As a result, the iron-containing samples completely overwhelm any contribution by the copper ions. If any additivity could be observed, it would be seen only at low iron concentrations. No synergistic effect was observed.

6.2 Continuous Observation of LGP1846 Decomposition by Measuring Pressure Rise.

Table 21. The Simultaneous Influence of Iron and Copper Ions on the Decomposition of LGP1846.

Ion concentration in ppm iron copper		Decomposition time in days
0	0	90.8
1	1	55.7
1	2	54.3
2	0	51.9
0	2	66.2
2	1	50.2
2	2	44.6
3	7	33.1
7	3	26.9
5	0	27.9
0	5	53.7
5	5	28.3
10	0	17.4
0	10	41.6
10	10	19.2
20	0	13.7
0	20	38.0

6.2.1 The Effect of Metal Ions on the Storage Life of LGP1846. The pressure cells, described in detail in Section 4.2, were used to study the effect of metal ions on propellant storage life. Pressure-time curves to a final pressure of 4 bar were recorded for samples stored at 90° C. The curves were compared with those obtained using pure liquid propellant. The time required to reach the final pressure is defined as the "lifetime" of the propellant. After termination of the test, the concentrations of HAN, TEAN, NH_4NO_3 , and HNO_3 in the sample were determined titrimetrically.

An increase in storage temperature from 90° C to 95° C was considered but abandoned. Spontaneous, vigorous decomposition occurred in samples that contained the less reactive Ni^{2+} and Co^{2+} ions, and pressures of over 50 bar were obtained, resulting in destruction of the pressure sensors.

In a number of samples, a pressure decrease of approximately 0.1 bar was observed during the first 24 hours of storage. This negative pressure excursion disappeared during the next 24 hours of

the test sequence. The samples in which this phenomenon was seen either contained less than 1 ppm of metal ions or other substances that did not strongly affect storage life. We suspect that the observation is caused by the depletion of oxygen in the containers through reaction with the propellant, followed by the more usual production of decomposition gases. The phenomenon was not included in evaluation of the graphical data.

We made use of the experience gained in the ampoule tests by initially studying only low concentrations of the most reactive ions together with pure propellant as reference. We also tested several of the less reactive ions of metals that are frequently used as alloying components in stainless steel.

Table 22 contains the analytical data obtained from samples containing 10 ppm of V, Fe, or Cu together with the pure propellant data stored under the same conditions. The marked influence of the three ions is readily recognized by shortened sample life. Ammonium nitrate and nitric acid appear as reaction products. The pressure is generated by decomposition of approximately 5% of the HAN TEAN decomposition is low in this test regime. The effect of iron, copper, and vanadium concentration on decomposition is presented in Tables 23, 24, and 25, respectively. Storage life is clearly dependent on the concentration of the different ions, and concentrations as low as 1 ppm have a considerable effect. No clear relation between metal ion concentration and composition of the sample residue can be derived. The time required to achieve the 4 bar final pressure as a function of metal ion concentration is shown in Figure 13. Vanadium is more reactive than iron, and copper is the least reactive of the three metal ions tested.

Figure 14 presents the gas production rate of pure propellant and of several samples containing 10 ppm of various metal ions. The uniform progression of the pressure-time curves caused us to expect that the sample residues should be similar in composition, but the data do not confirm this supposition. From information given in the relevant literature (Klein 1976), we may assume that the different metal ions react via different reaction mechanisms generating different reaction products as well. *[EDITOR'S NOTE: The data presented in Tables 23, 24, and 25 support the contention that the decomposition reaction mechanism is dependent on the specific metal ion that contaminates the propellant. The nitrogen content of LGP1846 is 20.16%. After storage at 90° C to achieve a pressure of 4 bar, the nitrogen content of the liquid residue is 19.93%, a decrease of 0.23%, and it is assumed that the gas generated contains the nitrogen lost. The residues of the samples containing iron show an average decrease in nitrogen of 0.24%, a difference so close to that of the uncontaminated propellant as to be within experimental error, and it is, therefore, presumed that the composition of the product gases is quite similar to that of the products from uncontaminated propellant. This is not the case when the contaminating ion is either copper or*

Table 22. Analytical Results of LGP1846 Contaminated With Metal Ions After Storage at 90° C in the Pressure Recording Apparatus.

Metal Ions (10 ppm)	Storage Time up to 4 bar (in days)	pH 1 : 1 dil.	NH ₄ NO ₃ in %	HNO ₃ in %	HAN in %	TEAN in %
Without Metallic Ions	42.5	0.57	1.79	1.36	54.37	17.02
Fe ²⁺	8.2	0.22	2.41	2.07	55.23	18.76
Cu ²⁺	12.0	0.39	3.29	2.11	54.08	20.45
V ⁴⁺	7.3	0.42	1.71	1.60	56.58	18.60

Table 23. The Influence of Iron Ions on the Storage Life of LGP1846.

Iron Concentration in ppm	Storage Time in days	pH 1 : 1 dil.	NH ₄ NO ₃ in %	HNO ₃ in %	HAN in %	TEAN in %
0	42.5	0.57	1.79	1.36	57.37	17.02
1	31.2	0.56	2.10	1.61	56.33	17.33
2	22.6	0.28	2.03	1.49	56.55	18.09
3	18.9	0.26	1.94	1.52	56.81	18.35
5	13.6	0.32	1.90	1.83	56.39	17.84
10	8.2	0.22	2.41	2.07	55.23	18.76

Table 24. The Influence of Copper Ions on the Storage of LGP1846.

Copper Concentration in ppm	Storage Time in days	pH 1 : 1 dil.	NH ₄ NO ₃ in %	HNO ₃ in %	HAN in %	TEAN in %
0	42.5	0.57	1.79	1.36	57.37	17.02
1	37.4	0.50	1.96	1.46	56.95	17.71
2	32.9	0.52	1.60	1.39	56.93	18.79
3	31.1	0.44	1.81	1.56	56.37	19.09
5	21.1	0.46	2.65	2.02	55.2	20.32
10	12.0	0.39	3.29	2.11	54.08	20.45

Table 25. The Influence of Vanadium Ions on the Storage of LGP1846.

Vanadium Concentration in ppm	Storage Time in days	pH 1 : 1 dil.	NH ₄ NO ₃ in %	HNO ₃ in %	HAN in %	TEAN in %
0	42.5	0.57	1.79	1.36	57.37	17.02
1	27.6	0.50	1.51	1.39	56.63	18.67
2	18.8	0.53	1.56	1.49	56.83	18.69
3	15.6	0.50	1.56	1.52	56.78	18.70
5	10.4	0.47	1.66	1.58	56.52	18.74
10	7.3	0.42	1.71	1.60	56.58	18.60

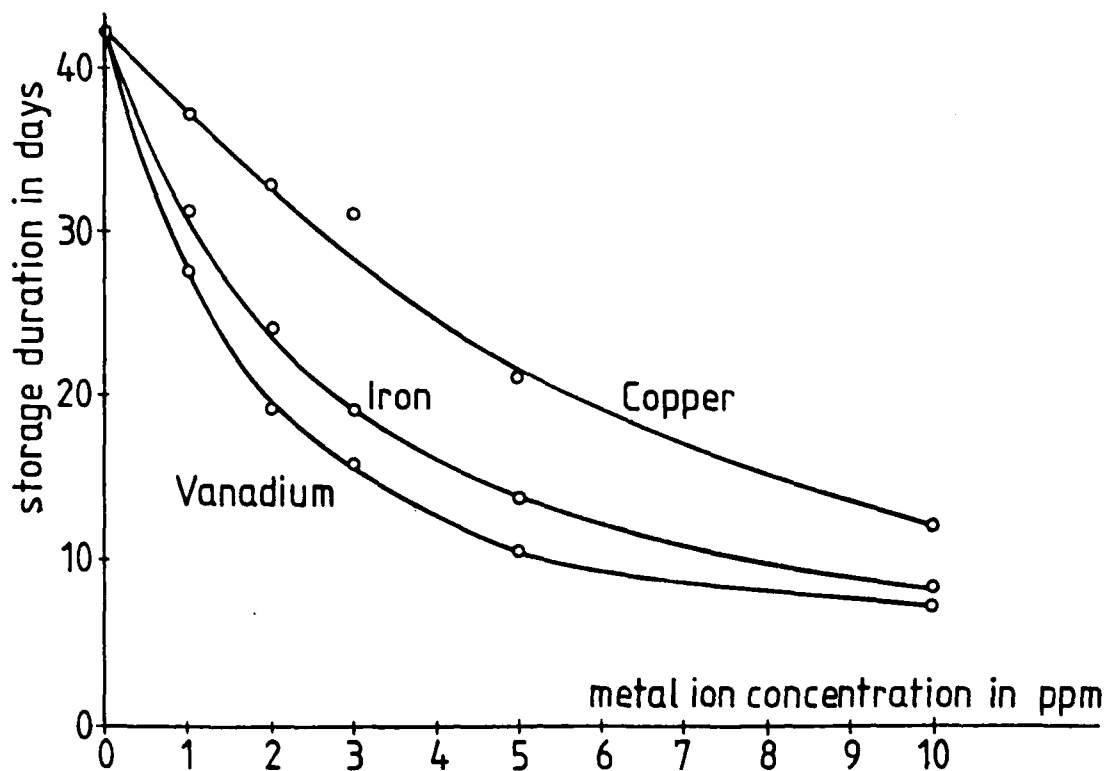


Figure 13. Storage Life of LGP1846 as a Function of Metal Ion Concentration.

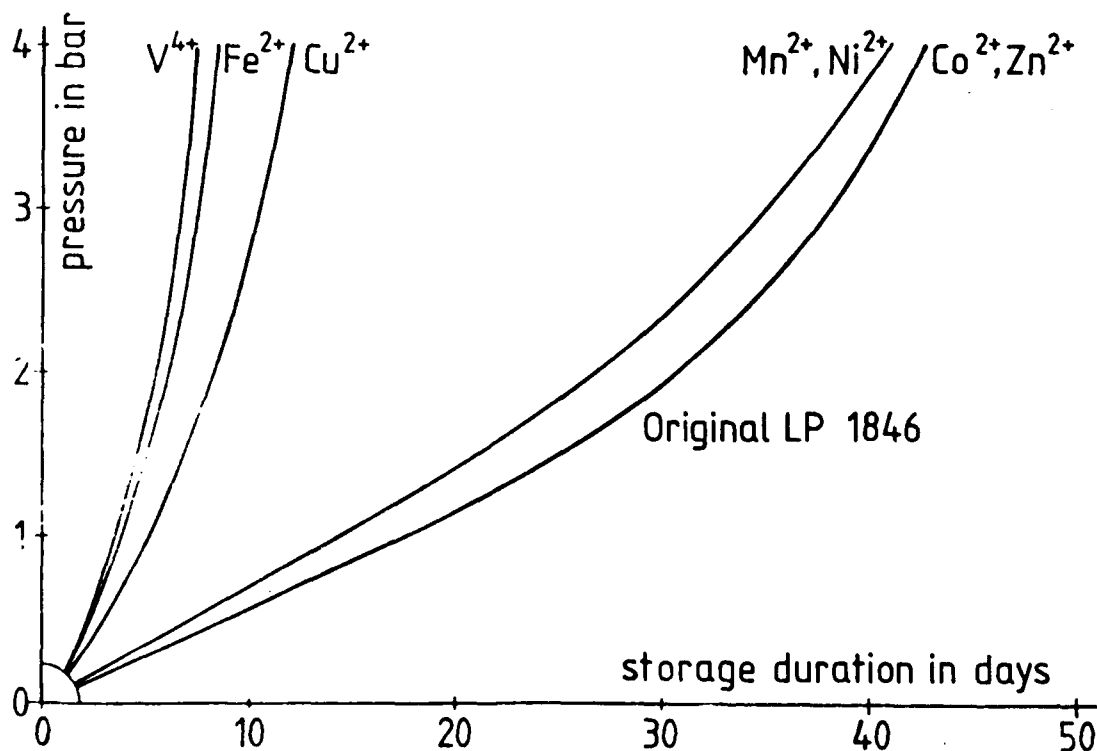


Figure 14. Pressure-Time Curves of Contaminated LGP1846. Metal Ion Concentration is 10 ppm.

vanadium. In the case of copper, the decrease in nitrogen content is 0.12%, significantly less than for uncontaminated samples, whereas the presence of vanadium produces a decrease of 0.25%. It must therefore be presumed that the composition of the product gases is different, and in the case of copper, that the molecular weight of the product gases is substantially lower. It is unfortunate that no analytical data for the product gases were furnished by the authors. Klein (1976) does contain product gas composition data and shows major differences between the iron and copper reactions. The experimental conditions under which the Klein (1976) data were obtained are so different from those used in the present work that little basis for comparison exists.] The ammonium nitrate data, especially in the presence of Cu ions, support this contention since, as seen in Table 24, more than 3% ammonium nitrate appears as a reaction product. [EDITOR'S NOTE: The ammonium nitrate data are particularly interesting. The production of NH_4^+ requires reduction of NH_3OH^+ . Since the only species present that can act as a reducing agent is NH_3OH^+ , an internal oxidation-reduction reaction must be postulated. It would seem from Table 24 that this reaction is enhanced by the presence of Cu^{2+} .]

6.2.2 The Influence of Stabilizers on the Storage Life of LGP1846. Tests of stabilizing additives, especially in the presence of iron ions, were reported in Section 6.1.4. The most effective additive found, Dequest 2041, was then chosen for further testing in the pressure measurement apparatus. Samples containing 10 ppm iron and Dequest 2041 in 1:10 molar ratio were compared with samples of pure propellant and propellant containing 10 ppm iron. The data obtained are shown in Figure 15. The presence of Dequest 2041 increases the time required to achieve 4 bar pressure from 8 to 31 days, a significant improvement although still less than the 42 days required to achieve the same pressure with uncontaminated propellant. Analytical data for the sample residues from these tests are given in Table 26. The quantities of ammonium nitrate and nitric acid obtained are similar to the amounts obtained in uncontaminated propellant.

[EDITOR'S NOTE: The nitrogen content of the Dequest containing residue is 19.98% having been reduced less than the 19.93% obtained with uncontaminated propellant stored under the same conditions. Gas production, as shown in Figure 15, appears to parallel the iron-free sample for approximately 15 days after which it breaks away and increases rapidly. This seeming inconsistency in the data together with the unusual shape of the pressure-time curve shown in Figure 15 raises the suspicion that the addition of Dequest 2041 to the sample does more than merely complex and make unavailable the iron present. It is possible that either Dequest 2041 or the iron-Dequest complex is thermally unstable at the test conditions employed and that the decomposition products obtained react with the propellant resulting in a reaction sequence different from the one observed with either pure or iron-contaminated propellant.]

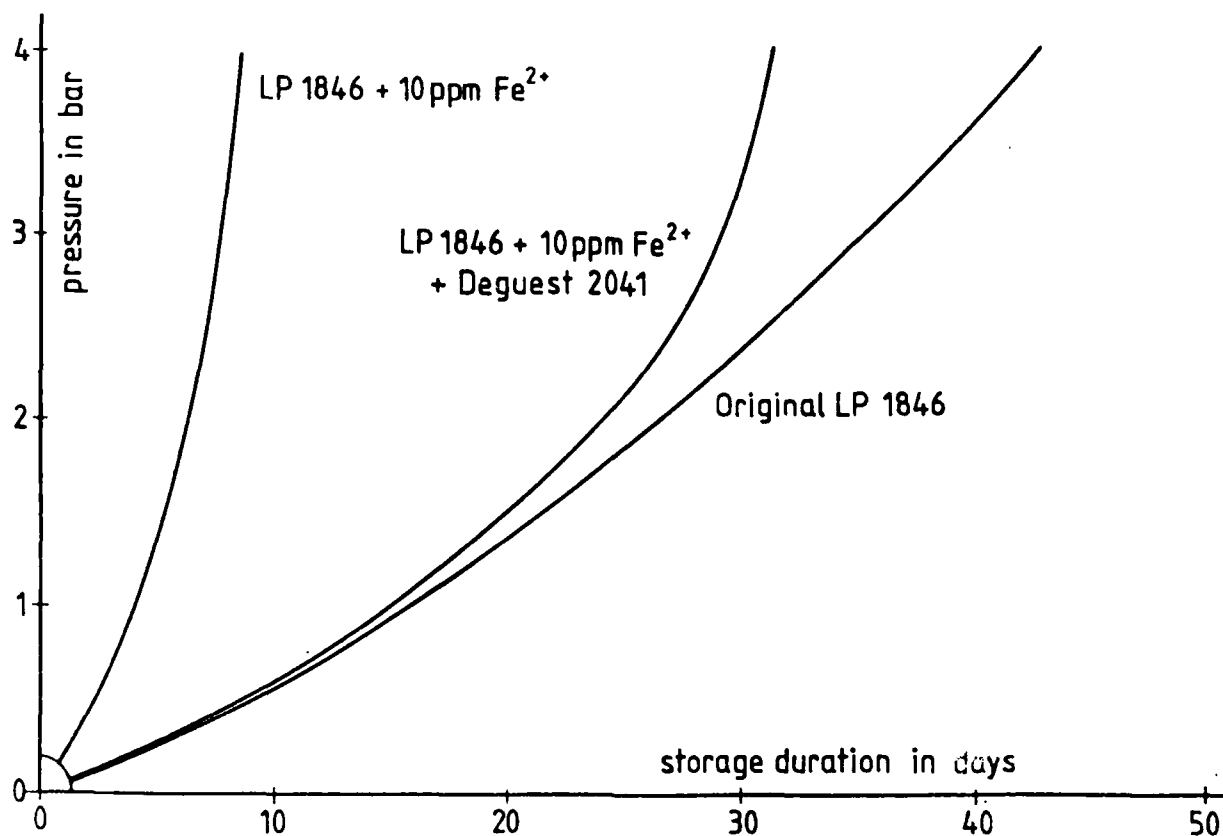


Figure 15. The Effect of Deguest 2041 on Gas Production Rates.

Table 26. Analytical Data for the Figure 15 Samples.

Addition	Storage Time up to 4 bar (in days)	pH 1 : 1 dil.	NH ₄ NO ₃ in %	HNO ₃ in %	HAN in %	TEAN in %
Without Fe ²⁺ (10 ppm)	42.5	0.57	1.79	1.36	57.37	17.02
Fe ²⁺ (10 ppm)	8.2	0.22	2.41	2.07	55.23	18.76
Fe ²⁺ (10 ppm) + Deguest 2041 Molar ratio (1:10)	31.5	0.53	1.61	1.64	56.35	19.66

These initial results are encouraging, although we must take into consideration that the storage life of pure propellant is considerably greater than that of samples to which metal ions and stabilizers were added. In spite of this, the objective of providing propellants with added protection against decomposition due to impurities should be pursued further. In assessing the value of stabilizers, E. Freedman, formerly of the BRL, was of the opinion that a storage temperature of 90° C shows the effect of these stabilizers in a disproportionately bad light (Freedman 1988) and that lower storage temperatures such as 65° C would be more suitable and realistic.

7. SUMMARY

Hydroxylammonium nitrate (HAN) is the substance most capable of reaction in the HAN-based propellants, decomposing into gaseous compounds. Decomposition is enhanced by the presence of specific impurities, and this property formed the starting point of our studies on the stability of the HAN-based propellants. Long-term storage at high temperatures in pressure containers was a particularly suitable method for testing the stability of these liquids. Two methods are described: (1) storage to rupture in sealed glass ampoules, and (2) storage to a specified pressure in glass containers equipped with pressure sensors.

The time required to achieve a specified pressure provides a sensitive parameter for assessment of the effects of impurities on storage life. Simultaneously, potentiometric titration methods were developed for quantitative determination of the concentration of components and decomposition products in propellant samples.

Three families of reaction could be distinguished when the liquid propellant LGP1846 came in contact with pure metals:

- (1) A number of metals such as antimony, rhenium, iron, and copper cause the propellant to decompose vigorously and the metals dissolve.
- (2) Other metals such as zinc and manganese are dissolved by the propellant without apparently influencing its storage life.
- (3) Finally, we find metals such as gold, silver, and tantalum, which are neither attacked nor reduce stability. These metals are suitable as materials of construction.

A number of steel alloys produce considerable decomposition. The propellant showed particularly low stability in the presence of two gun steels. Among the polymers examined, only polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE) remained stable and did not adversely affect the stability of the propellant. Other sealing materials were severely attacked and accelerated the decomposition of the propellant to an extent equal to that of the steel alloys tested.

Metal ions, present in the propellant as impurities, also affect storage life. Apart from the well-known, and very conspicuous effect of copper and iron ions, an appreciable effect was observed with vanadium ions. Stability was adversely affected by vanadium compounds at concentrations as low as 0.5 ppm. At concentrations of less than 10 ppm, most other metal ions showed only a slight effect.

The thermal stability of LGP1846 is influenced by pH, and maximum stability was obtained within the pH range 1.9 to 2.7. The optimum pH value is at 2.1. All measurements were made with samples diluted 1:1 with water.

Many organic compounds are capable of forming chelation complexes with metal ions and could thus make the metal ions incapable of lowering propellant storage life. A number of aminophosphonic acids, most notably Dequest 2041, were able to increase the storage life of LGP1846 containing 10 ppm iron at 90° C from 17 to 47 days. Although the effect observed does not appear to be sufficient for practical purposes, it is encouraging and serves as motivation to carry out further research.

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